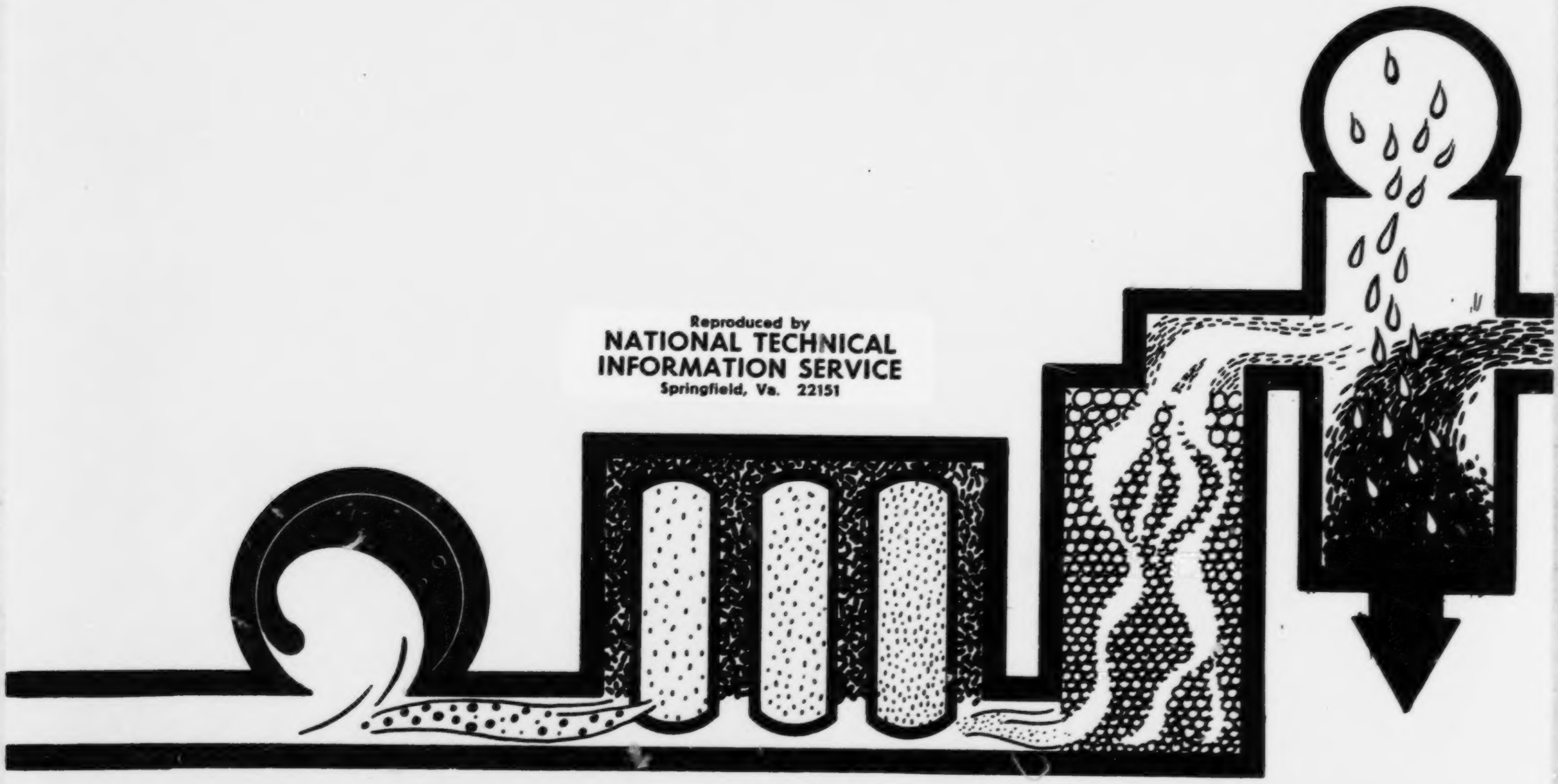
PB196735

CLEAN WATER WATER POLLUTION CONTROL RESEARCH SERIES ● ORD- 17010FKF12/69

W71- 03455

BASIC SALINOGEN ION-EXCHANGE RESINS FOR SELECTIVE NITRATE REMOVAL FROM POTABLE AND EFFLUENT WATERS

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151



U.S. DEPARTMENT OF THE INTERIOR • FEDERAL WATER QUALITY ADMINISTRATION

95

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Reports describe the results and progress in the control and abatement of pollution of our Nation's waters. They provide a central source of information on the research, development, and demonstration activities of the Federal Water Quality Administration, Department of the Interior, through in-house research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

Water Pollution Control Research Reports will be distributed to requesters as supplies permit. Requests should be sent to the Planning and Resources Office, Office of Research and Development, Federal Water Quality Administration, Department of the Interior, Washington, D. C. 20242.

1 Accession Number W71-03455	2 Subject Field & Group 05D	**SELECTED WATER RESOURCES ABSTRACTS** **INPUT TRANSACTION FORM**

5 *Organization*

Tyco Laboratories, Inc.,
Waltham, Mass~~achusetts [illegible]~~

6 *Title*

BASIC SALINOGEN ION-EXCHANGE RESINS FOR SELECTIVE NITRATE REMOVAL FROM POTABLE AND EFFLUENT WATERS,

10 *Author(s)*

A. L. Walitt
H. L. Jones

16 *Project Designation*

Program #17010 FKF,
Contract #14-12-439

21 *Note*

~~For~~ sale by the ~~Superintendent of~~ Documents, U. S. Government Printing Office, Washington, D. C. 20402
Price $1.00 I67.13/4:17010 FKF12/69 [illegible]

Available from the National Technical Information Service as PB 196 735, ~~[illegible] paper copy,~~ $0.95 in microfiche

22 *Citation*

Advanced Waste Treatment Research Laboratory,
Cincinnati, Ohio,
December, 1969.
Water Pollution Control Research Series ORD 17010 FKF 12/69,
88 p, 17 tab, 10 fig, 28 ref, 2 append

23 *Descriptors (Starred First)*

*Ion exchange, ~~nitrate ion, weak-base resin, resin synthesis, resin regeneration, water pollution, ion selectivity and capacity~~ *Waste water treatment, *Resins, Ions, Nitrates, Chlorides,

25 *Identifiers (Starred First)*

~~Nitrate-specific, weak-base, ion-exchange resins~~ *Nitrate ions, *Nitrate [illegible], Resin synthesis, Weak-base resins, Resin regeneration, Ion selectivity, Ion capacity, Styrenes, Chloride ions,

27 *Abstract*

Preparation of nitrate-specific ion-exchange resins, which incorporate selected primary amines grafted onto polystyrene, has been investigated. The best selectivity for nitrate ion over chloride ion was obtained with the 1-naphthylmethl-aminomethyl derivative of polystyrene (1-NMA resin). Nitrate was adsorbed quantitatively from feed solutions containing five times as much chloride ion as nitrate ion. Under identical conditions, commercial weak-base resins removed only 70% of the nitrate ion.

The 1-NMA resin could be regenerated repeatedly in the chloride form by HCl, but attempts at alkaline regeneration led to irreproducible results. Recommendations for future work include investigation of the effects of cross-linking, addition of hydrophilic functional groups, quaternization of the amine, and incorporation of different, nitrate-selective, functional groups. ( )

Abstractor ~~A. L. Walitt~~ H. L. Jones	Institution

WR:102 (REV. JULY 1969)
WRSIC

SEND TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

* GPO: 1969-359-339

BASIC SALINOGEN ION-EXCHANGE RESINS FOR SELECTIVE NITRATE REMOVAL FROM POTABLE AND EFFLUENT WATERS

by

A. L. Walitt
H. L. Jones

Tyco Laboratories, Inc.
Waltham, Massachusetts 02154

for the

FEDERAL WATER QUALITY ADMINISTRATION
DEPARTMENT OF THE INTERIOR

Program #17010 FKF
Contract #14-12-439
FWQA Project Officer, R. H. Wise
Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio
December, 1969

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price $1

FWQA Review Notice

This report has been reviewed by the Federal Water Quality Administration and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Federal Water Quality Administration, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Preparation of nitrate-specific ion-exchange resins, which incorporate selected primary amines in polystyrene, has been investigated. The best selectivity for nitrate ion over chloride ion was obtained with the 1-naphthylmethylaminomethyl derivative of polystyrene (1-NMA resin). Nitrate was adsorbed quantitatively from feed solutions containing five times as much chloride ion as nitrate ion. Under identical conditions, commercial weak-base resins removed only 70% of the nitrate ion.

The 1-NMA resin could be regenerated repeatedly in the chloride form by HCl, but attempts at alkaline regeneration led to irreproducible results. Recommendations for future work include investigation of the effects of cross-linking, addition of acidic functional groups, quaternization of the amine, and incorporation of different, nitrate-selective, functional groups.

This report was submitted in fulfillment of Program No. 17010 FKF and Contract No. 14-12-439, under the sponsorship of the Federal Water Quality Administration.

Key Words: Ion exchange, nitrate ion, weak-base resin, resin synthesis, resin regeneration, water pollution, ion selectivity and capacity.

CONTENTS

Page No.

Section

I CONCLUSIONS 1

II RECOMMENDATIONS 3

III INTRODUCTION 5

IV DISCUSSION 11

V REFERENCES 31

Appendix

I SYNTHETIC APPROACHES 33

II DETAILED NOTES ON EXPERIMENTAL WORK 45

ILLUSTRATIONS

Figure No. Page No.

1. Ratio of Effluent Concentration to Influent Concentration, C/C_0, as a Function of Throughput (in Bed Volumes) 18

2. Effluent Nitrate-Ion Concentration as a Function of Throughput (Numbers in Parentheses Are pH Values; $C_0 = 5.6 \times 10^{-3}$M, Bed Volume = 25 ml) 63

3. Effluent Chloride-Ion Concentration as a Function of Throughput ($C_0 = 2.8 \times 10^{-2}$M, Bed Volume = 25 ml) 64

4. Ratio of Effluent Concentration to Influent Concentration, C/C_0, as a Function of Throughput (in Bed Volumes) for the 1-NMA Resin (Influent Contains 0.0056M Nitrate Ion and 0.028M Chloride Ion) 67

5. Ratio of Effluent Concentration to Influent Concentration, C/C_0, as a Function of Throughput (in Bed Volumes) for Rexyn 203 (Influent Contains 0.0056M Nitrate Ion and 0.028M Chloride Ion) 68

6. Ratio of Effluent Concentration to Influent Concentration, C/C_0, as a Function of Throughput (in Bed Volumes) for Duolite A7 (Influent Contains 0.0056M Nitrate Ion and 0.028M Chloride Ion) 69

7. Ratio of Effluent pH to Influent pH (pH/pH_0) as a Function of Throughput (in Bed Volumes) for Rexyn 203 71

8. Ratio of Effluent Concentration to Influent Concentration, C/C_0, as a Function of Throughput (in Bed Volumes) for the 1-NMA Resin (Influent Contains 0.00161M Nitrate Ion and 0.0082M Chloride Ion) 75

ILLUSTRATIONS (Cont.)

Figure No. Page No.

9. Ratio of Effluent Concentration to Influent Concentration, C/C_0, as a Function of Throughput (in Bed Volumes) for Rexyn 203 (Influent Contains 0.00161M Nitrate Ion and 0.0082M Chloride Ion) 76

10. Ratio of Effluent Concentration to Influent Concentration, C/C_0, as a Function of Throughput (in Bed Volumes) for Duolite A7 (Influent Contains 0.00161M Nitrate Ion and 0.0082M Chloride Ion) 77

TABLES

No.		Page
I	Capacities and Selectivity Coefficients for Nitrate Over Chloride of Resins Derived From Chloromethylated Polystyrene and Selected Primary Amines	14
II	Selectivity Coefficient of 1-NMA Resin at Various, Initial, Nitrate and Chloride-Ion Concentrations	15
III	Resin-Regeneration Material Balances	20
IV	Adsorption and Release of Nitrate Ion,Using 3 g of 1-NMA Resin	21
V	Acid Regeneration of 1-NMA Resin [Resin Sample Prepared From Mixed(2%, 4%, 8%) Divinylbenzene-Cross-Linked Polystyrene]	22
V-a	Acid Regeneration of 1-NMA Resin [Resin Sample Prepared From 1%-Divinylbenzene-Cross-Linked Polystyrene]	23
VI	Weak-Base Capacities of Synthesized Resins	52
VII	Capacities and Selectivity Coefficients of Resins Derived From Chloromethylated Polystyrene and Selected Primary Amines	59
VIII	Selectivity Coefficients for 1-Naphthylmethyl Resin at Various, Initial, Nitrate-Ion and Chloride-Ion Concentrations	60
IX	Selectivity Coefficients for Rexyn 203, Duolite A7, and Synthetic 1-Naphthylmethyl Resin at Various Ionic Fractions	61
X	Physical Properties of Resin Columns	66
XI	Material Balance of Regeneration Effluents	72
XII	Physical Properties of Resin Columns	73
XIII	Acid-Exchange Cycles of 1-NMA Resin	83
XIV	Regeneration of Spent 1-NMA Resin With HCl	85

TABLES (Cont.)

No. Page

XV Nitrate-Ion Uptake From Neutral Solutions 85

XVI Acid Regeneration of 1-NMA Resin Prepared From 1% DVB-Cross-Linked Polystryrene 87

XVII Breakthrough Experiments: 1-NMA Resin (1% DVB), Rexyn 203, and Duolite A7 88

SECTION I

CONCLUSIONS

Nitrate-specific, ion-exchange resins have been developed, using the concept that certain functional groups, incorporated into polystyrene, can show high selectivity. Certain amines known to yield insoluble nitrate salts were chosen as basic functional groups for these resins.

Ten, different, primary amines were reacted with chloromethylated polystyrene to yield secondary-amine, weak-base, anion-exchange resins. The capacity of these resins and their selectivity for nitrate ion over chloride ion were measured and compared with two, commercial, anion-exchange resins. The capacities of the synthesized resins ranged from 0.98 to 2.67 meq/g, and their selectivity varied from 1.4 to 14. The best selectivity was obtained with the 1-naphthylaminomethyl derivative of polystyrene (1-NMA resin), and this resin was therefore investigated in more detail.

The selectivity of 1-NMA resin for nitrate ion over chloride ion ranged from 7.5 to 14, depending on the ionic strength of the feed. Nitrate ion was adsorbed quantitatively from feed solutions containing five times as much chloride as nitrate ions. Under identical conditions, the commercial weak-base resins (Rexyn 203 and Duolite A7) removed only 70% of the nitrate ion.

The 1-NMA resin could be regenerated in the chloride form by 1N HCl. Several exchange/regeneration cycles were accomplished without loss of nitrate-ion capacity. However, attempts to regenerate the 1-NMA resin using alkaline solutions led to irreproducible results, sometimes with loss of capacity. A similar resin, prepared with lower cross-linking to increase swellability, appeared to have as good ion-exchange properties and showed the possibility of easier regeneration.

From this work, we have concluded that it is possible to make a nitrate-selective, ion-exchange resin. Although not all possible functional groups showing strong nitrate interactions have been investigated, the best resin obtained thus far can achieve quantitative removal of nitrate ion from a solution comparable to wastewater.

SECTION II

RECOMMENDATIONS

Future research and development, on the preparation of nitrate-specific ion-exchange resins, are indicated by the present study. Topics to be investigated should include:

Cross-Linking: Reduced cross-linking of the polystyrene increases the swellability of the resin and can therefore increase the rate of ion exchange and regeneration. Resins containing as little as 1% divinylbenzene should be investigated.

Acidic Functional Groups: In addition to the primary amine group, the incorporation of acidic groups, such as $-SO_3H$ and $-COOH$, should markedly improve the resin's hydrophilicity. The zwitterionic nature of these derivatives in neutral solution may increase the ability of the resin to split salts.

Quaternization of the Amine: Conversion of the secondary amine group in the resin to a quaternary ammonium ion will increase the ability of the resin to split salts and may, at the same time, allow it to retain its selectivity for nitrate ion.

Other Functional Groups: Incorporation of other structures which may possess nitrate selectivity should be investigated (e.g., nitron and N, N-diethylbenzohydrylamine).

The results of the present research program have shown the essential feasibility of the proposed concept and have indicated that further work could result in the development of an efficient material for the removal of nitrate ion from wastewaters. It is strongly recommended that work in this area be continued.

Preceding page blank

SECTION III

INTRODUCTION

BACKGROUND

The contamination of streams and waterways with relatively low concentrations of nitrate ion continues to be a problem in areas where there are sizable quantities of agricultural runoff water. The nitrate concentration derives from the extensive use of fertilizers in agricultural areas since inorganic, soluble nitrates are washed out by irrigation waters into the local waterways. Concentrations of nitrate ion generally range from 20 to 100 mg/l in the runoff, with considerably higher concentrations of other inorganic ions, such as chloride, sulfate, and bicarbonate.

The presence of nitrates in inland waterways and bays sets in motion a series of events (e.g., extensive algae growth and cessation of aerobic bacterial growth) which may lead to the eutrophication of the water system. The decay of plant life, along with the flourishing of anaerobic bacterial growth, ultimately leads to fish-kills and possibly to the total destruction of water quality. In a report[1] by the FWQA, the conclusion is reached that the nitrate concentration of discharge waters must be reduced to less than 9 mg/l in order to prevent serious contamination by algae growth.

Another consequence of the high concentration of nitrate in drinking water is the susceptibility of some infants to methemoglobinemia. This disease, which occurs in certain children during the first few months of their lives, is the result of the chemical reduction of nitrate to nitrite within the intestine (instead of either to nitrogen or to ammonia, as occurs in adults). Nitrite ion may combine with hemoglobin in the blood and render it unavailable as an oxygen carrier, in much the same manner as does carbon monoxide. Nitrates have been known to be transmitted to infants through breast milk or cow's milk, and the disease is relatively common in infants in areas where the use of nitrate-containing fertilizers is extensive.[2]

Surveys are being made of the occurrence of nitrate in well-water, [3] but at present its removal is not considered economically feasible. Availability of an inexpensive method for removal of nitrate at the 20- to 100-mg/l concentration level would permit use of water supplies not now available. Removal of nitrate from wastewaters would substantially reduce algae growth in lakes and streams.

Preceding page blank

ALTERNATIVE PROCESSES

A variety of processes has been investigated for the economical removal of nitrate from wastewaters. Probably the most successful and advanced of these processes has been developed largely through the inhouse efforts of the Taft Center, FWQA.[4,5] This process entails the biological denitrification of wastewater in a manner somewhat analogous to conventional, activated-sludge, secondary treatment of wastewater. A high rate, carbon-oxidation step is followed by a nitrification process in which all fixed-nitrogen species, including organic nitrogen and ammonia, are converted to nitrates; then, the nitrates are bacteriologically converted to nitrogen by a denitrification process. This procedure has shown high promise of success. Overall fixed-nitrogen removals as high as 85% have been obtained. There was some difficulty in process control, however, since the management of a three-sludge system proved somewhat unwieldy.

Another process under limited investigation (and use) entails the controlled growth of algae in ponds to reduce the nitrate concentration, with subsequent filtration of the plant life prior to discharge of the water. This method is now in use in the delta region of San Francisco, acting upon San Joaquin River Basin runoff water. Difficulties are being encountered with the efficiency of filter systems and the required frequency of backwashing.

Other processes, entailing methods for catalyzed chemical reduction of the nitrates to ammonia or to nitrogen, have been proposed. For example, electrochemical reduction of nitrate to ammonia, followed by air stripping, has been considered.

An alternative approach which has been considered for nitrate removal is the use of chemical precipitants, with separation of the nitrate-containing, solid phase from the nitrate-free liquid. In general, the inorganic nitrate salts are much too soluble to be considered as precipitants. However, certain synthetic, organic bases form nitrates which are almost water-insoluble,[6,7] and these have been utilized for quantitative analysis of soluble nitrates.

Such chemical-precipitant processes uniformly suffer from the high, continuing cost of additive chemicals which renders these processes too expensive for use with the extremely high volume of nitrate-contaminated waters encountered in agricultural regions.

Anion exchange has also been considered as a nitrate-removal technique.[1] Available anion-exchange resins, however, are not highly selective for nitrate. As a result, the effective capacity of the resin is quite small, and despite the elimination of continuing chemical-additive costs, the initial investment required for resin is too high to be economical. It has been estimated that, with presently available ion-exchange resins, the cost of treating an average of 100 million gal./day would be \$42/acre-ft of water, based on a 50-year, 3 1/8% amortization. This estimated cost is arrived at after a credit of almost \$10/acre-ft is assumed from the recovery of ammonium nitrate for use as fertilizer.

The same study has shown that a hypothetical resin with a selectivity of 20 for nitrate over chloride (a resin which would operate on waters in the pH range 7 to 8) would yield treated water at a cost of \$11/acre-ft, assuming the same plant size, amortization schedule, and credits. Unfortunately, the assumed amortization schedule is unrealistic in today's money market.

It is clear that a nitrate-specific, anion-exchange resin is sorely needed. If such a resin operated on the hydroxide or carbonate cycle, the cost of replenishing an expensive organic compound would be replaced by the cost of purchasing an inexpensive regenerant. Furthermore, no contamination of the product water by organic substances would occur.

THE TYCO, NITRATE-SPECIFIC, ION-EXCHANGE PROCESS

The advantages of a highly specific, anion-exchange resin in reducing the cost of nitrate removal from agricultural wastewaters were pointed out in the preceding section. Tyco Laboratories undertook the development of a nitrate-specific, ion-exchange resin by combining the concept of a chemical precipitant with that of an ion-exchange resin. Specifically, the research covered the incorporation, as part of an ion-exchange resin, of a specific functional group known to be particularly selective for nitrate ion when that functional group is utilized as a monomer. The basic idea is an extension of the work of Skogskeid,[8] who synthesized a polystyrene-resin derivative containing dipicrylamine groups (dipicrylamine as a monomer is known to be a specific precipitating agent for potassium cations). The resulting resin was found to be specific for adsorption of potassium ions.

The basic salinogens are a group of nitrogenous substances which form complex, insoluble, crystalline compounds with inorganic nitrates by virtue of coordinate valencies. Chelate-ring considerations apply to these compounds, as they do to the well-known acidic reagents for cation complexing (namely EDTA), but no replaceable hydrogen is needed. The best known of the basic salinogens is nitron (I) (4, 5-dihydro-1, 4-diphenyl-3, 5-phenylimino-1, 2, 4-triazole), which has been used for gravimetric nitrate determination.[9] Other members of the salinogen group include N, N-diethylbenzohydrylamine (II), di-(1-naphthylmethyl)-amine (III), and α-phenyl-β-diethylaminoethyl-p-nitrobenzoate (IV). Each of these organic bases has somewhat different properties. Compound III is said to be better than nitron as a nitrate precipitant,[7] and IV is as good as nitron as a gravimetric reagent.[10]

Nitron is reported to be water-insoluble, although nitron nitrate is very slightly soluble in dilute acid solution.[9] Compounds such as III, as well as nitron formate (fornitral), have nitrates much less soluble than nitron. It is apparent from previous work that effective precipitation of nitrate at the 50-mg/l level can be accomplished. With fornitral, for example, immediate nitrate precipitation is obtained from cold water containing 30 mg/l of nitric acid; while a visible precipitate is obtained after 5 hr with as little as 7.5 mg/l of nitric acid.

Since the salinogen nitrates are soluble to the extent of 0.001% to 0.01%, it is desirable to eliminate any possibility of loss of the amine (with corresponding contamination of the treated water) by incorporating it into an ion-exchange resin. This technique has been used for the development of specific cation-exchange resins, but it does not appear to have been applied, as yet, to anion exchange. One example of such work is that of Skogskeid,[8] previously cited. Other examples of the incorporation into resins of functional groups which form chelates with metal ions are known. For example, anthranilic acid[10] is known to form a specific ion-exchanger for zinc. Iminodiacetic acid is also the basis of Dowex A-1, a commercially available, chelating resin.

Compounds that form insoluble nitrates contain weak-base, secondary or tertiary amine groups, and these should be incorporated readily into polystyrene resins. Quaternary amines may also have nitrate sensitivity. Well-known, anion-resin-formation reactions may be utilized in the formation of salinogen resins.[11] These reactions involve chloromethylation of polystyrene with chloromethyl ether, followed by reaction with the amine to give the hydrochloride of the corresponding methyl-aminated styrene. Combination of a usable synthetic method with the amines that are specific nitrate precipitants should result in the formation of an anion-exchange resin especially adapted to low-level nitrate removal from water.

An additional factor that must be considered in the development of a nitrate-specific, ion-exchange resin is the relation between specificity and exchange rate. Because of the introduction of groups with which the nitrate ion will tend to associate, its mobility in the resin tends to be reduced. Thus, the gain in selectivity may be accompanied by a loss in exchange rate. This effect will require a compromise between complete selectivity with a low exchange rate, and low selectivity with a high exchange rate. These factors, in turn, will dictate the choice of salinogen base attached to the resin and the maximum allowable concentration of amine; i.e., the maximum exchange capacity that can be built into a nitrate-selective resin.

Other anions also precipitated by nitron include perchlorate, perrhenate, pertungstate, and fluoroborate. None of these is present in supply or effluent water at a level that would cause appreciable reagent consumption over that equivalent to the nitrate. In the case of borate, some waters may contain it at levels high enough to make its removal desirable. (The nitrate-selective resins may also remove borates.)

OBJECTIVE OF THIS PROGRAM

In the light of the preceding remarks, the goal of this research program was to make use of a variety of practical, synthetic-organic reactions in order to form a solid-phase, salinogen reactant which would operate as a nitrate-specific, ion-exchange resin at the pH of the nitrate-containing feed water. The nitrate-containing water would be passed through a bed containing the solid salinogen resin. The nitrate would be exchanged with resin hydroxide or carbonate ions. After the nitrate-removal capacity of the resin had been exhausted, it would be regenerated with concentrated alkali, such as Na_2CO_3 or NaOH. The nitrate would thus be recovered as a relatively concentrated solution of $NaNO_3$ which may be usable as a fertilizer. The regenerated salinogen resin would then be used for further nitrate removal.

SECTION IV

DISCUSSION

SUMMARY OF WORK DONE UNDER THIS PROGRAM

Choice of Resins: Shortly after the inception of the program in July, 1968, two papers[12, 13] were found which reported the sensitivity (defined by the minimum nitrate-ion concentration which would yield a precipitate with a given reagent concentration) of a group of amines for the precipitation of nitrate ion, and the corresponding selectivity with regard to other common, inorganic ions. A series of amines which appeared to have the highest selectivity for nitrate ion was thus chosen.

It was considered that the criterion of sensitivity, although extremely important with regard to precipitation by monomers, was not as important when the nitrate-removing reagent was a polymer . The true criterion for nitrate adsorption by a polymer should be the affinity of the polymer for the ion. In the case of the monomer, there may well be stong interactions to form a nonionized compound which remains soluble, such as occurs with weak acids. Such a monomer will be a poor precipitant for nitrate. However, when it is built into a polymer, where the insolubility is inherent, the same functional group could be an excellent nitrate remover, provided that it maintains its high affinity for nitrate. Therefore, the principal criterion for the choice of amine derivatives of polystyrene to be synthesized was the selectivity for nitrate over other common, inorganic ions.

The Importance of Selectivity: Selectivity is an extremely important criterion for the utility of an ion-exchange material, insofar as the objectives of the present contract are concerned. Nitrate ion almost invariably appears in relatively low concentrations; e.g., from 20 to 100 mg/l in agricultural runoff waters. Invariably, in the same waters there are concentrations of chloride and sulfate which far exceed that of the nitrate ion. Chloride is often present in quantities up to 1000 mg/l, and sulfate often up to 200 mg/l and sometimes greater.

Ordinarily, ion-exchange resins of the weak-base type are considerably more selective for sulfate and other divalent ions than they are for either nitrate or chloride. Furthermore, the selectivity of conventional, weak-base, ion-exchange resins is only slightly greater for nitrate than for chloride. Therefore, in a wastewater which is predominately sulfate- and chloride-containing, with only small concentrations of nitrate ion, any ion-exchange resin will become saturated after having adsorbed only miniscule

Preceding page blank

quantities of nitrate. On the other hand, if a weak-base resin can be synthesized with a functional group which has high selectivity for nitrate ion, it will then be possible to utilize high proportions of the resin's active sites in the removal of nitrate ion from solution prior to their saturation and subsequent need for regeneration. The effect of high selectivity is illustrated in the following examples of resins having selectivities of 1 and 100 for nitrate over chloride ion. The selectivity, S, is identical to the equilibrium constant for the exchange reaction:

$$\textcircled{P}^{+}Cl^{-} + NO_3^{-} \rightleftharpoons \textcircled{P}^{+}NO_3^{-} + Cl^{-} \qquad (1)$$

$$S = K = \frac{[\textcircled{P}^{+}NO_3^{-}]\,[Cl^{-}]}{[\textcircled{P}^{+}Cl^{-}]\,[NO_3^{-}]} \qquad (2)$$

where $\textcircled{P}^{+}$ is the ammonium form of the aminated, cross-linked polystyrene — the stationary phase. If we assume that the chloride-ion concentration in a wastewater is five-fold greater than the nitrate-ion concentration, then, if the selectivity of the resin for nitrate is 1 (which represents equal affinity of the polymer for nitrate and for chloride), the resin becomes completely spent when:

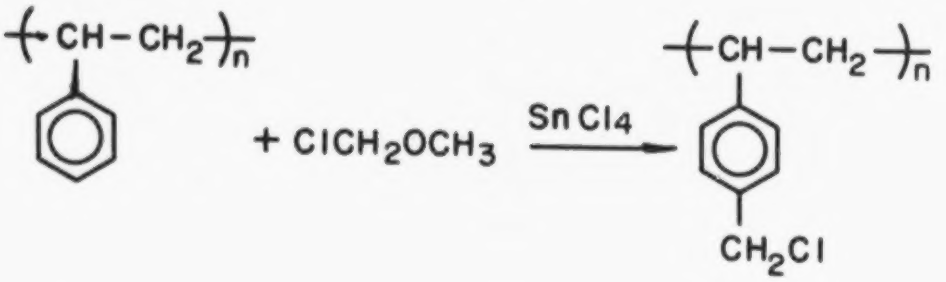
$$\frac{[\textcircled{P}^{+}NO_3^{-}]}{[\textcircled{P}^{+}Cl^{-}]} = S\,\frac{[NO_3^{-}]}{[Cl^{-}]} = (1)\,\frac{1}{5} = 0.20 \qquad (3)$$

That is, only 20% of the resin will be converted to the nitrate form before regeneration is necessary. On the other hand, if the selectivity of the resin is 100, its utility under similar conditions is:

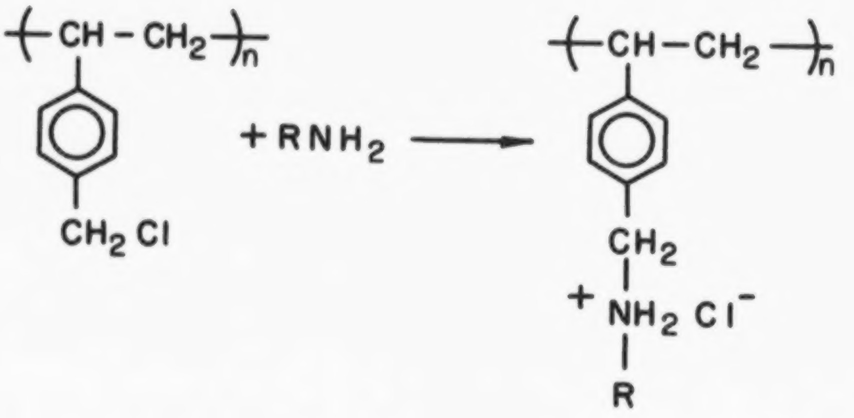
$$\frac{[\textcircled{P}^{+}NO_3^{-}]}{[\textcircled{P}^{+}Cl^{-}]} = (100)\,\frac{1}{5} = 20$$

That is, approximately 95% of the resin will have been converted to the nitrate form before the resin is spent and regeneration is necessary. The effective capacity of the resin is directly proportional to its selectivity. It becomes clear, then, that high selectivity is an extremely important requirement.

Screening for Selectivity: The work which has been carried out to date has proved to be highly promising for the achievement of an ion-exchange resin with high selectivity and high capacity for nitrate ion. A number of ion-exchange resins based on one of the polymer systems proposed were prepared. All resins prepared were weak-base derivatives of polystyrene. The starting material was reticulated beads of divinylbenzene-cross-linked polystyrene which consisted of equal quantities of resins containing 2%, 6%, and 8% divinylbenzene. Polystyrene was treated with chloromethylether to form the p-chloromethyl derivative of polystyrene, as illustrated below. Analysis of the product indicated that approximately 80% of the phenyl groups had been chloromethylated in this procedure. This yield was in good agreement with literature values.

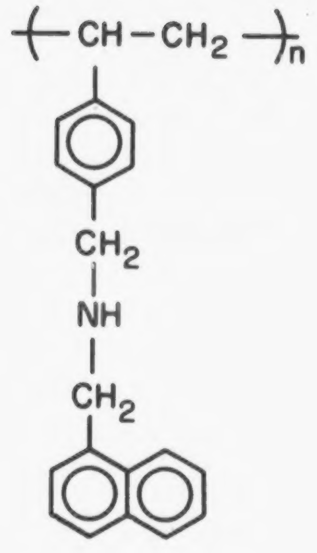


The chloromethylated polymer was reacted in a series of separate reactions with selected primary amines in dioxane solution. A large excess of each primary amine was used in order to reduce the probability of forming tertiary amine derivatives of the polymer. The capacity of each of the products, as well as the selectivity coefficient for nitrate over chloride ions, was determined. The reaction between chloromethylated polymer and a primary amine (to form the desired, secondary-amine derivatives) is



The primary amines used are listed in Table I, along with their respective capacities and selectivity coefficients for nitrate over chloride, both of which are compared with those of the commercial, weak-base, ion-exchange resins, Duolite A7 and Rexyn 203.

Note that, of the amines prepared (as listed in Table I), all demonstrated significant selectivity for nitrate over chloride. Several of the derivatives of these resins demonstrate a significant superiority over the selectivity coefficients of the commercially available, weak-base resins. One resin in particular, the 1-naphthylmethylaminomethyl derivative of polystyrene



(which we will henceforth refer to as 1-NMA resin), exhibits a far greater selectivity coefficient than any of the others. This interesting observation is in keeping with the work of Hutton,[12,13] discussed earlier.

Table I. Capacities and Selectivity Coefficients for Nitrate Over Chloride of Resins Derived From Chloromethylated Polystyrene and Selected Primary Amines

Primary Amine	Capacity, meq/g	Selectivity Coefficient, S
Benzyl	2.25	2.7
4-Chlorobenzyl	1.69	7.6
4-Methoxybenzyl	2.17	3.1
1-Naphthylmethyl	1.85	14.0
Isopropyl	2.59	7.0
n-Butyl	2.67	1.4
t-Butyl	2.51	7.0
n-Hexyl	0.98	6.4
Cyclohexyl	2.21	6.7
n-Octyl	1.07	4.3
Duolite A7	7.00	3.8
Rexyn 203	4.94	4.7

The secondary amine, benzyl-1-naphthylmethylamine (which is a monomeric analogue of 1-NMA resin), showed a solubility for its nitrate salt of 0.697 g/l at 21 °C. By comparison, the hydrochloride salt of the same amine had a solubility of 38.36 g/l. This demonstrates extremely high selectivity for nitrate over chloride ions in the case of this amine. Hutton also reported that the limiting concentration of nitrate ion for precipitation was 5 mg/l. The selectivity of benzyl-1-naphthylmethylamine was considerably greater than that of di-(1-naphthylmethyl)-amine, for which the nitrate solubility was 0.093 g/l and the hydrochloride solubility was 0.46 g/l at 21 °C. However, the sensitivity of the latter was greater, as demonstrated by the lower solubility of its nitrate salt.

Of all the secondary amines tested by Hutton, the benzyl-1-naphthylmethylamine was chosen as the most useful for the precipitation of nitrate ion, from the standpoints of both selectivity and sensitivity. It is therefore hardly surprising that the discovery was made in this work that the 1-NMA resin, which contains precisely the same functional group, was found to be the most highly selective for absorption of nitrate over chloride.

The selectivity coefficient of the 1-NMA resin at various, initial, nitrate and chloride concentrations was determined in a series of batch tests. It was found that the sensitivity of the resin varied quite markedly with variation in initial nitrate and chloride concentrations, as shown in Table II.

Table II. Selectivity Coefficient of 1-NMA Resin at Various, Initial, Nitrate and Chloride Ion Concentrations

$[NO_3^-]_{initial}$, mol/l	$[Cl^-]_{initial}$, mol/l	S
0.031	0.1	8.7
0.032	0.05	7.5
0.017	0.05	12.5
0.057	0.05	14.0

There is little information in the literature on the variation of selectivity with total ionic concentration. Almost invariably, the selectivity is reported at constant, total, ionic concentration. Furthermore, the total ion concentration is chosen so that the total number of ions in the equilibrating solution is equal to or less than the number of active exchange sites in the resin. We are reasonably certain, therefore, that the variation in selectivity shown in Table II is not unusual.

Similar variations in the selectivity of the commercial resins, Duolite A7 and Rexyn 203, were also observed in identical experiments. In a series of experiments covering a wide range of initial nitrate and chloride concentrations, selectivity coefficients ranging from 7.5 to 14.0 for nitrate over chloride were observed for the 1-NMA resin (see Table II). However, over the same range of initial nitrate and chloride concentrations, the selectivity coefficicients (for nitrate over chloride) of Duolite A7 ranged from 1.9 to 3.8, and of Rexyn 203 from 1.7 to 4.7. It is thus clear that the 1-NMA resin exhibits considerably higher selectivity for nitrate than do commercial, weak-base, ion-exchange resins. By this determination, the precept on which this work was based has been proved. Unusually high selectivity can be built into an ion-exchange resin by the expediency of choosing active exchange groups which, as monomers, are known to interact selectively with a given ion.

Continuous Exchange Experiments: The validity of the selectivity concept was therefore established, and one resin was prepared which was shown to have considerably greater selectivity than other synthesized, or commercially available, weak-base resins. The high selectivity was then demonstrated over a wide range of initial ion concentrations; after this, it had to be demonstrated that the resin could be used in a realistic situation with suitable regeneration capability. For this purpose, larger quantities of resin were prepared. Initial exchange experiments were carried out with an aqueous solution containing relatively high concentrations of both chloride and nitrate ions [990 mg/l (0.028M) chloride ion, and 350 mg/l (0.0056M) nitrate ion]. The acidity of the feed water was maintained at pH 2.

The continuous exchange experiments were carried out using similar beds of synthesized 1-NMA resin, Rexyn 203, and Duolite A7. All were in the free-base form. In each case, the bed was 2 cm in diameter and 8 cm high. However, because of the considerable differences in volume capacity of the three resins, the total capacities of the beds were:

1-NMA:	18 meq
Rexyn 203:	30 meq
Duolite A7:	50 meq

Under the given operating conditions, the 1-NMA resin almost completely removed the nitrate from approximately 45 bed volumes of feed solution. The effluent finally reached the original nitrate concentration of the influent after about 65 bed volumes. By comparison, Rexyn 203 from the beginning removed 70% of the nitrate in the feed (i.e., from the very beginning of the experiment, about 30% of the nitrate from the original solution came through in the effluent). In addition, about 25% of the chloride in the original solution was also removed. This situation remained static over about 160 bed volumes. At this point, the concentrations of both nitrate and chloride in the effluent gradually increased until they became equal to that of the effluent after about 200 bed volumes. In the case of Duolite A7, approximately 65% of the nitrate and 25% of the chloride were removed over approximately 180 bed volumes, with the concentration of the effluent finally equaling that of the influent after approximately 240 bed volumes. The comparison in nitrate-absorption capacity of Rexyn 203 and Duolite A7 with that of the 1-NMA resin is demonstrated clearly in Fig. 1.

An extremely interesting set of conclusions, which demonstrated that the sum of the takeup of nitrate and of chloride by both Rexyn 203 and Duolite A7 was equivalent to the takeup of hydrogen ion, was derived from these breakthrough experiments. Beginning with the free-base form of each resin, only that quantity of nitrate or chloride which corresponded to the formation of a salt form of the resin could be adsorbed. Thus, it was found that throughout the life of Duolite A7 and Rexyn 203, as they adsorbed nitrate and chloride, the pH of the effluent water was approximately 9 compared to a pH of 2 for the influent water. The takeup of nitrate from influent water is therefore closely related to the acidity of that water; hence, for Rexyn 203 and Duolite A7 to have any utility, it will always be necessary to acidify the influent water quite strongly.

In the case of the synthesized 1-NMA resin, the pH of the effluent water was equal to that of the influent water after only 4 bed volumes, despite the fact that the resin continued to take up nitrate ion quantitatively for more than 45 bed volumes. Thus, it became clear that the adsorption of nitrate ion was not necessarily related to the adsorption of hydrogen ion from solution, and that the resin demonstrated unusual affinity for nitrate. At this point, the suspicion arose that the observed result was not the classical behavior of a weak-base resin in a solution containing inorganic anions. The affinity of the 1-NMA resin for nitrate ion was considerably higher than we expected for a weak-base resin.

Regeneration: Once it was demonstrated that the affinity of the 1-NMA resin for nitrate ion was unusually high, we undertook the regeneration of the resin with the intent that long-term life-tests for the resin would be carried out. We intended to cycle the resin, alternating adsorption of nitrate with subsequent regeneration to determine the utility of this unique anion-exchange resin.

At this point, difficulties began to arise in what appeared to be an otherwise successful program. It was discovered that regeneration of the resin was extremely erratic: sometimes it was achieved completely, sometimes incompletely, and sometimes not at all. Indeed, it began to ap-

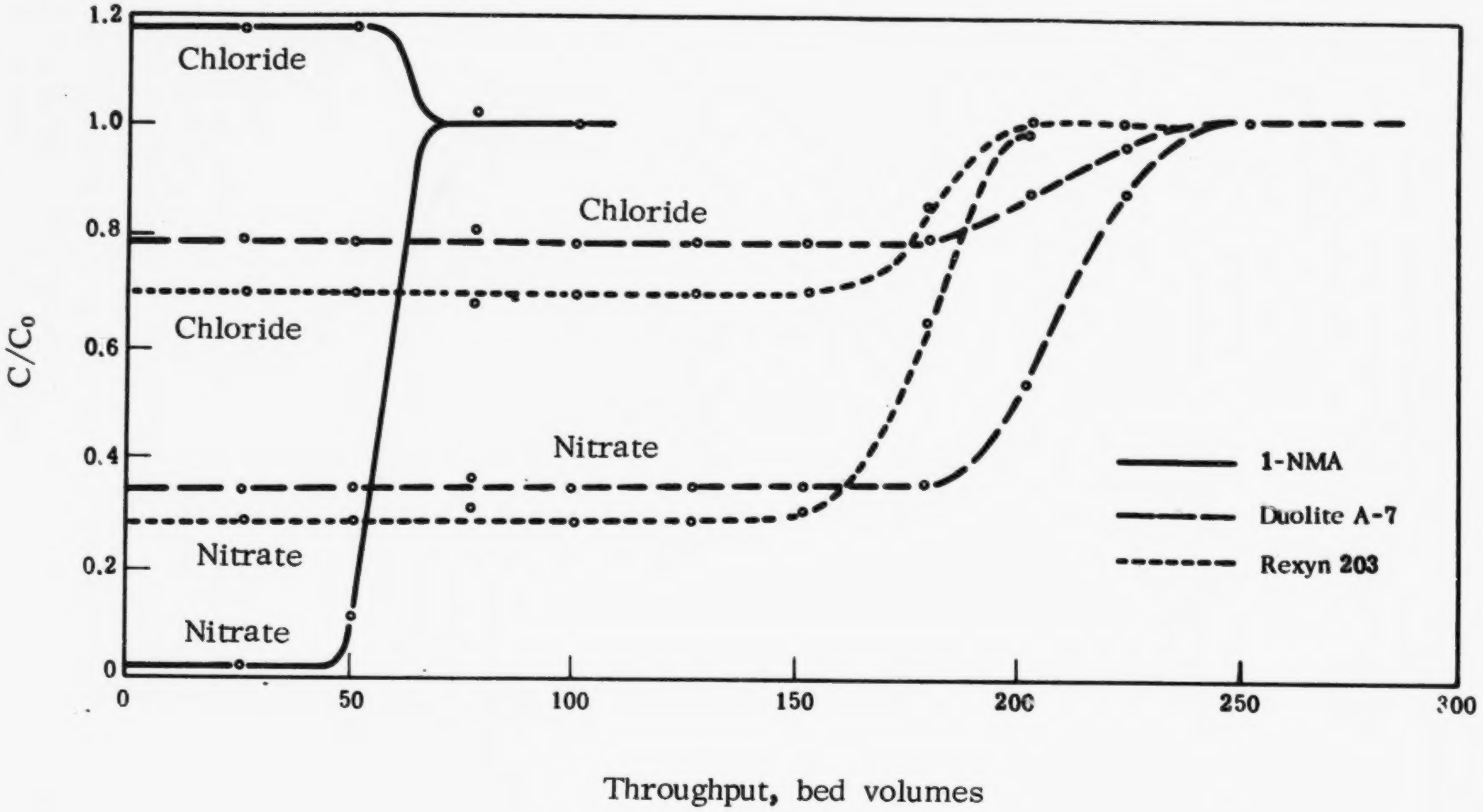


Fig. 1. Ratio of effluent concentration to influent concentration, C/C_0, as a function of throughput (in bed volumes)

pear that the affinity of the 1-NMA resin for nitrate was so high that regeneration under reasonable operating conditions, and by conventional techniques, could not be achieved.

It is well known that conventional, weak-base resins will not "split" salts. That is, in the free-base form, the resin will have no effect on a neutral solution of an inorganic salt. Conversely, the resin in the salt form will be hydrolyzed by water at pH greater than pK_b, where K_b is the basicity constant of the resin. However, if the resin is converted to its salt form by the addition of strong acid, it will act as an anionic exchanger. The reactions of the resin may then be written as:

$$R\overset{+}{N}H_2\,Cl^- + NO_3^- \rightarrow R\overset{+}{N}H_2\,NO_3^- + Cl^- \qquad (5)$$

and

$$R\overset{+}{N}H_2\,Cl^- + H_2O \rightleftharpoons RNH \cdot H_2O + H^+\,Cl^- \qquad (6)$$

In strongly acidic solutions, Eq. (6) is driven to the left. Even in neutral solutions, the kinetics of Eq. (6) are much slower than those of Eq. (5), and a high degree of exchange capacity may be usable before appreciable quantities of active sites are rendered inactive by the hydrolysis.

The proportion of the resin which can be utilized by a given anion is in accordance with its selectivity for the various anions. When the conventional, weak-base resin becomes spent, it can be regenerated by the addition of water (which generates the free-base form); then, the addition of strong acid regenerates the salt form. The generation of the free base is effected more readily as the pH of the regenerating solution is increased.

In order to be absolutely certain that regeneration of the 1-NMA resin would occur, it was treated with 500 ml of 1.25M sodium hydroxide (20 bed volumes). Although the resin had taken up 8.5 meq of nitrate ion during the breakthrough experiment, only 2.5 meq of nitrate was found in the regenerating solution. Addition of 1.25M sodium hydroxide solution released no further nitrate ion. The observed effect is demonstrated in Table III, with comparisons of similar experiments with Rexyn 203 and Duolite A7.

The high quantity of chloride which appeared to be taken up by the Rexyn 203 and the Duolite A7 is considered to be spurious because the total quantity of (chloride + nitrate) adsorbed is considerably greater than the known total capacity of the quantities of resins used. Since the recovered nitrate corresponds closely to the adsorbed nitrate, it is likely that the chloride is in error. In the case of the 1-NMA resin, although 8.5 meq of nitrate was taken up (approximately equal to the total capacity of the column), only 2.5 meq was released upon regeneration. Virtually no chloride was present in the spent resin since no chloride was taken up and only very small quantities were released.

Table III. Resin-Regeneration Material Balances

	Total Adsorption,* meq		Total Regeneration,† meq	
Resin	Nitrate	Chloride	Nitrate	Chloride
1-NMA	8.5	—	2.5	0.90
Rexyn 203	20.0	31.0	18.0	14.8
Duolite A7	19.0	36.5	15.0	22.0

---

*From a solution containing 990 mg/l chloride and 350 mg/l nitrate, at pH 2, until the resin was spent.

†By a 1.25M sodium hydroxide solution until no further ions were eluted.

We have spent considerable time attempting to discover ways for efficient regeneration of the free-base resin once the hydronitrate has been formed, but without reproducible success to date. Attempts included successive treatment by solutions of ammonium hydroxide, sodium bicarbonate, sodium carbonate, and aqueous sodium hydroxide. The results are given in Table IV.

In our regeneration experiments, alcoholic potassium hydroxide solution was no more successful than was aqueous sodium hydroxide solution. Also, note from Table IV that the effective capacity of the resin diminishes with each cycle.

Although we were not completely successful in using alkaline media to regenerate the resin in its free-base form, we were able to use HCl to regenerate it in the chloride form. The results of a series of treatments of two different resin beds are given in Table V and Va. After the initial conversion of the highly cross-linked resin (first resin bed) to the chloride form, subsequent wash cycles with HCl and HNO_3 resulted in a constant uptake of Cl^-. This shows that the resin may be regenerated in the hydrochloride form, and that it may be recycled without loss of capacity. The nitrate-ion uptake in treatments nos. 10 and 14 was close to the preceding chloride-ion uptake,

Table IV. Adsorption and Release of Nitrate Ion Using 3 g of 1-NMA Resin

Reactant	Column Feed		Adsorption, meq	Release, meq
	Concentration	ml		
HCl	1N	250	—	—
HNO_3	0.113N	550	4.8 NO_3^-	4.9 Cl^-
NH_4OH	1N	100		2.8 NO_3^-
NH_4OH	1N	320		0.1 NO_3^-
$NaHCO_3$	1N	182		0.01 NO_3^-
Na_2CO_3	1M	90		0.01 NO_3^-
NaOH	1.25N	100		0.01 NO_3^-
HNO_3	0.113N	125	3.3 NO_3^-	
NaOH	1.25N	168		0.03 NO_3^-
NH_4OH	1N	153		0.4 NO_3^-

Table V. Acid Regeneration of 1-NMA Resin [Resin Sample Prepared From Mixed (2%, 4%, 8%) Divinylbenzene-Cross-Linked Polystyrene]

Treatment No.	Column Feed,[*] ml			Ion Uptake, meq/g		Ion Release, meq/g	
	HCl	H_2O	HNO_3	Cl^-	NO_3^-	Cl^-	NO_3^-
1	790	—	—	1.6	—	—	3.48[†]
2	—	50	—	—	—	0.30[‡]	—
3	—	—	175	—	1.60[§]	1.91	—
4	100	—	—	0.69[§]	—	—	0.97[†]
5	—	25	—	—	—	0.17	—
6	—	—	125	—	n.d.	0.92	—
7	—	25	—	—		—	0.20
8	100	—	—	0.61	—	—	0.74
9	—	25	—	—	—	0.26	—
10	—	—	100	—	0.77	0.93	—
11	—	25	—	—	—	—	0.14
12	100	—	—	0.69	—	—	0.58
13	—	25	—	—	—	0.16	—
14	—	—	125	—	0.68	0.84	—
15	—	25	—	—	—	—	0.16
16	100	—	—	0.80	—	—	0.69

---

[*] All acid wash solutions were 0.1M

[†] In the absence of a preceding water wash, ion release included residual, interstitial solution from the previous treatment. This value is significant in treatment no. 1 since the prior treatment had been with 1N $NaNO_3$.

[‡] The "ion released" value in a water wash is expressed as meq/g and is probably attributable to residual, interstitial solution from the prior treatment, although some hydrolysis of the weak-base group may also be occurring. The sum of these two values is generally small compared to the capacity.

[§] Note that in treatment no. 3, 1.6 meq/g of nitrate was taken up. However, on subsequent hydrochloride regeneration (treatment no. 4), only 0.69 meq/g of chloride was adsorbed. We believe that not enough hydrochloric acid regenerant solution had been used in this step.

Table V-a. Acid Regeneration of 1-NMA Resin [Resin Sample Prepared From 1%-Divinylbenzene-Cross-Linked Polystyrene]

Treatment No.	Column Feed		Ion Uptake		Ion Release	
	Species	ml	Species	meq/g	Species	meq/g
1	H_2O	250	—	—	—	—
2	HCl (3N)	100	—	—	—	—
3	HCl (1N)	100	—	—	—	—
4	H_2O	25	—	—	—	—
5	$NaNO_3$	100	NO_3^-	1.40	Cl^-	1.60
6	H_2O	25	—	—	NO_3^-	0.39
7	HCl (1N)	100	—	—	—	—
8	H_2O	50	—	—	—	—
9	$NaNO_3$	100	NO_3^-	1.40	Cl^-	1.38
10	H_2O	40	—	—	NO_3^- Cl^-	0.37 0.02
11	HCl (3N)	100	—	—	—	—
12	HCl (1N)	25	—	—	—	—
13	H_2O	25	—	—	Cl^- NO_3^-	0.73 0.01
14	$NaNO_3$	100	NO_3^-	1.35	Cl^-	1.61
15	H_2O	25	—	—	NO_3^-	0.43
16	HCl (3N)	100	—	—	—	—
17	HCl (1N)	25	—	—	—	—
18	H_2O	25	—	—	Cl^- NO_3^-	0.80 0.01
19	$NaNO_3$	100	NO_3^-	1.36	Cl^-	1.63
20	H_2O	25	—	—	NO_3^- Cl^-	0.43 0.01

which supports this statement.

The possibility of chloride regeneration is substantiated when we consider the results for the 1%-cross-linked resin (second resin bed). Here, nitrate-ion uptake was constant for four complete cycles, while chloride-ion release was constant for three of the four cycles. The lower value of chloride ion released in treatment no. 9 was probably due to more interstitial chloride ion being washed out in treatment no. 8 (50 ml of water wash instead of 25 ml).

Unfortunately, HCl regeneration is not economically feasible. The recovered nitrate is in a hydrochloric acid solution, from which it would be difficult to reclaim as a salable product.

Apparently, the simple, inexpensive methods normally used for regeneration of ion-exchange resins have not been successful in regenerating 1-NMA resins. It appears that we have chosen to examine in depth a specific example of the proposed concept which was far too successful; that is, the affinity of the 1-naphthylmethylamine group (in the polystyrene resin) for nitrate ion is so great that regeneration to the free base by ordinary methods is unsuccessful.

Over a large number of exhaustion and regeneration cycles, concentrated caustic solutions were least successful in regenerating the resin, despite the known fact that weak-base resins are generally more readily regenerated as the pH is increased. It appeared, furthermore, that the resin was more readily converted from the hydronitrate form to the hydrochloride form by 0.1N to 3N HCl solutions than by more concentrated acid solutions. There appeared to be more success in regeneration at moderately low pH than at either high pH or extremely low pH.

Because of the quite unusual behavior of the 1-NMA resin, compared to other, known, weak-base resins, consultative assistance was sought from Professor Harry Gregor, Professor of Chemical Engineering, Columbia University. Professor Gregor's achievements in the development of ion-exchange resins and membranes are well known, and he has worked extensively in the development of ion-specific resins. A detailed examination of the extensive exchange data of 1-NMA resin led to a series of conclusions which, we believe, is consistent with the observed facts.

The erratic behavior of 1-NMA resin with regard to regeneration may be related to the difficult swellability of the final resin. Two separate factors contribute to this undesirable property for an ion-exchange resin.

Factor 1: The polystyrene raw material, which was made available to us by Dow Chemical Company early in the program, was rather highly cross-linked (a mixture of equal quantities of 2%, 6%, and 8% divinylbenzene-cross-linked polymer). With such a high degree of cross-linking, the polymer is able to swell to a maximum of only two to three times its dry volume in dioxane or in any other solvent which might be used. Subsequent to the swelling, the polystyrene was reacted with chloromethylether; then, the resultant chloromethylated polymer was reacted with 1-naphthylmethylamine which introduces a new group into the polymer. This new group is approximately as large as the pores or interstices which were created in the polymer by the swelling process. The introduction of the large,new group causes physical strains in the polymer and shatters the original beads. It was indeed observed in virtually all synthesis experiments that the introduction of the naphthylmethylamine group reduced the resin form from a reticulated bead to a fine powder. Thus, the resin no longer had an open structure since the interstices were filled with the added group. Furthermore, because of the relatively high degree of cross-linking, the polymer could be swelled no further to accommodate both the new, large group and also reasonable quantities of water. With so tight a structure and so little water content, the accessibility of exchange sites is very poor and is strongly dependent on small changes in swelling introduced by changes in total ionic strength or in pH. Thus, these sites are virtually inaccessible to solutions of very high or very low pH since the high ionic strength tends to withdraw water from the resin particles by osmosis. The sites are somewhat more readily accessible to solutions of moderate pH and moderate ionic strength. Thus, regeneration by strong acid or base solutions could not be effected.

Factor 2: The difficulty in swellability, inherent in the geometry of the resin, is further enhanced by the fact that the newly introduced 1-naphthylmethylamine group introduces a high degree of hydrophobicity into the resin. The naphthylmethyl group itself is highly hydrophobic and will introduce this property into any molecule in which it is present.

A further consequence of the poor swelling of the original styrene and of the chloromethylated styrene was the poor accessibility of the active chloromethyl groups to 1-naphthylmethylamine during the amination reaction. As a consequence, relatively poor yields have been achieved. At best, capacities of 1.75 to 2.25 meq/g were observed, despite a theoretical capacity of 2.75 meq/g based on the degree of chloromethylation, and 3.23 meq/g based on the original polystyrene.

Swellability would be expected to be increased by lower degrees of cross-linking in the polymer. Some last-minute experiments were run, using 1%-divinylbenzene-cross-linked polystyrene (obtained from Professor H. P. Gregor) to produce a new batch of 1-NMA resin. This resin was used in several cycles of nitrate adsorption and HCl regeneration. Solutions used in these experiments were neutral, dilute mixtures of nitrate and chloride, approximating the concentrations found in agricultural waters.

A series of breakthrough experiments was also run to compare the new (1% divinylbenzene) 1-NMA resin and the commercial resins, Rexyn 203 and Duolite A7. The solution to be treated contained 25 mg/l NO_3^- and 100 mg/l Cl^-. The new resin achieved 81.5% nitrate removal, compared to 58% for the commercial resins. These data indicate that, although the capacity of the 1-NMA resin is lower than the commercial resins, the new material is capable of producing effluents of lower nitrate content.

This series shows the expected improvement in capacity when sufficient HCl is used to regenerate the resin.

These considerations point to a direction for further development which would take advantage of the extremely high selectivities of 1-NMA resin for nitrate ion. At the same time, they may yield resins which possess active sites more readily available to a polluted water and which are also easily regenerable with conventional, inexpensive, regenerating agents.

DIRECTIONS FOR FUTURE RESEARCH

At this stage of development, the present program ended. Since there has been no funding to continue the work, in this section we will summarize our ideas for further possible research suggested by our results. The most immediate work to be done is covered by the following tasks, each of which will be discussed in more detail in the following paragraphs.

1. Samples of 1-NMA resins should be synthesized from 1%-divinylbenzene-cross-linked polystyrene, according to the methods which have proved successful in the preceding work.

2. A derivative of the 1-NMA resin should be synthesized with a sulfonic acid group in the five-position of the naphthalene ring.

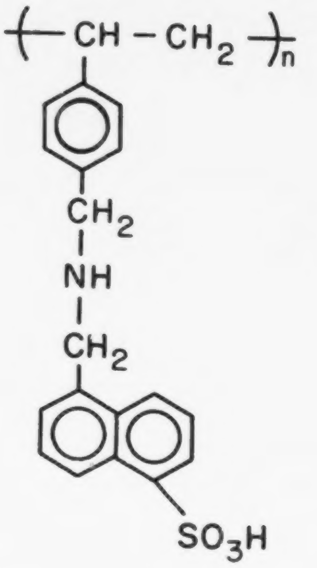
3. A new polystyrene-resin derivative should be prepared in which the substituted amine will be o-(t-butyl) -benzylamine. This amine is recommended for its steric properties. The synthesis method would be similar to that employed in paragraphs 1 and 2, above. The raw material is readily available.

4. Each of the above resins should be quaternized by reaction with methyl chloride or methyl sulfate.

5. Testing of each of these resins should be carried out in an ion-exchange column, using an aqueous solution containing 500 mg/l chloride ion and 100 mg/l nitrate ion at pH 7 as test solution.

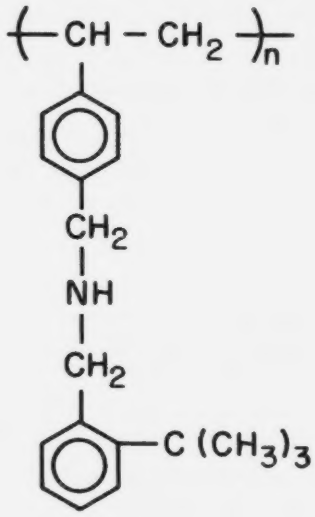
Reduced Cross-Linking: The polystyrene resin, which is utilized for preparation of the final 1-NMA resin and its derivatives, should be cross-linked by divinylbenzene to a degree no greater than 1%. The resin should be fully swollen (to as much as five to six times its original volume, if possible) by immersion in the reaction solvent for at least 24 hr. After reaction, the 1-NMA resin can be expected to remain swollen and thereby improve the exchange characteristics. Samples of the 1%-cross-linked polystyrene, although not readily available commercially, are made by a number of manufacturers (e.g., Nalco Chemical) and should be available for research purposes. As mentioned previously, initial tests on a 1-NMA resin made from a sample of 1%-divinylbenzene-cross-linked polystyrene showed improved ease of regeneration and better nitrate-removal capability when compared to more highly cross-linked materials and the commercial, ion-exchange resins. Future work on this aspect should receive highest priority.

Increased Hydrophilicity: To improve the accessibility of the ion-exchange groups to aqueous solutions, a hydrophilic substituent may be added to the naphthalene ring prior to its introduction into the resin. Specifically, the amination reagent (to be reacted with lightly cross-linked, chloromethylated polystyrene) would be 5-sulfo-1-naphthylmethylamine (a known dyestuff intermediate) which would yield the resin:



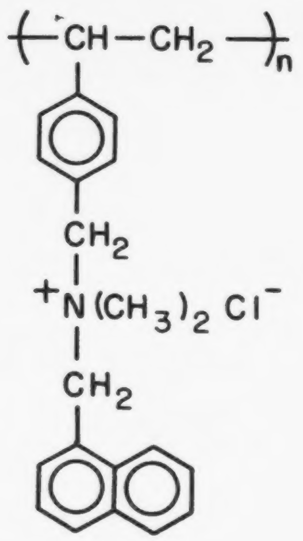
The sulfonic acid group would render the naphthyl substituent more hydrophilic and should yield a highly swollen resin, especially if 1%-cross-linked polystyrene serves as the starting material.

An alternative method for improving the hydrophilicity of the final resin would be the substitution of a smaller, but more hydrophilic, group for the naphthyl group; this would increase wettability while leaving the molecular bulk untouched. The structure of one resin which might achieve this result, by the introduction of o-(t-butylbenzyl), would be:



This structure may demonstrate as high a nitrate selectivity as does the analogous naphthylmethylamine derivative because of the similar effect of the t-butyl group on the structure of water in the vicinity of the secondary amine group. We are not in total agreement with this hypothesis which is based on the previously reported work of Hutton et al on the specificity of amine monomers; 1-naphthylmethyl-t-butylamine nitrate had a relatively high solubility compared to di-(1-naphthylmethyl) -amine nitrate. Therefore, this alternative should probably receive less priority than that outlined above.

Quaternization: Quaternization of the secondary amine group will yield the strong-base resin:



The advantage of a strong-base resin in place of a weak-base resin would be the ability of the former to take up inorganic ions from neutral solutions (that is, to "split" salts) without the competitive hydrolysis reaction. [Recall the discussion regarding the competitive reactions, (5) and (6), which may occur with weak-base resins in neutral solutions.] If the hydrolysis reaction, (6), is completely eliminated, as would be the case for a strong-base resin, the full capacity would be available for the exchange reaction (5).

Quaternization can be achieved by standard methods. Each of the resins is suspended in anhydrous methanol, and a methanolic solution of methyl sulfate is added. Gentle refluxing is sufficient to quaternize the amine group.

We suggest that 5-g quantities of each of the prepared resins be placed in a column for exchange experiments. Bulk experiments need not be carried out to determine specificity for any of these resins. Instead, the resins can be placed immediately into columns and treated with quantities of a simulated wastewater to determine their capacity and selectivity. The spent resins can be screened rapidly for their regenerability. If any of these resins give promise of real utility, their continued cycling over long periods of time can then be carried out. We believe that the evaluation of these additional resins should yield sufficient information for a relatively complete assessment of the utility of amine derivatives of polystyrene for the purpose of selected absorption of nitrate from wastewater.

It would also be desirable to examine the selectivity of these resins for nitrate over such ions as sulfate and bicarbonate, as well as over chloride. This latter aspect has not yet been examined.

We believe that the research carried out thus far under the present program has shown considerable potential for the eventual development of economically feasible, ion-exchange resins for removal of nitrate from wastewater. In a spirit of cooperation with future workers in the field, we have included two appendices in which considerable details of our synthesis and testing experiments are presented, and we hope that this line of research will not be abandoned ultimately.

SECTION V

REFERENCES*

1. "San Joaquin Master Drain," report by FWQA, Southwest Region (1967).

2. Wood, E. C., Proceedings of the Society of Water Treatment and Examination, 10, 76 (1961).

3. Larson, T. E., "Occurrence of Nitrate in Well Waters," Illinois State Water Survey, Champaign (1966).

4. Barth, E. F., *et al.*, J. Water Pollution Control Federation, 38, No. 7, 1208 (1966).

5. Barth, E. F., *et al.*, J. Water Pollution Control Federation, 40, No. 12, 2040 (1968).

6. Gutbier, A., Z. Angew. Chemie, 18, 494 (1905).

7. Konek, F., Z. Anal. Chem., 97, 416 (1934).

8. Skogskeid, A., U. S. Patents 2592349 and 2592350 (1952).

9. Welcher, F. J., "Organic Analytical Reagents," 3, Van Nostrand, New York (1947).

10. Gregor, H. P., Taifer, M., Citarel, L., and Becker, E. I., Ind. Eng. Chem., 44, 2834 (1952); and Marvel, C. S., and DuVigneaud, V., J. Amer. Chem. Soc., 46, 2661 (1924).

11. Helferich, F., "Ion Exchange," McGraw-Hill, New York (1962).

12. Hutton, R. C., Salam, S. A., and Stephen, W. I., J. Chem. Soc. (A), 1573 (1966).

13. Hutton, R. C., and Stephen, W. I., J. Chem. Soc. (A), 1426 (1967).

14. Fierz-David, H. E., and Blangey, L., "Grundlegende Operationen der Farbenchemie," Springer, Vienna (1943).

15. Busch, M., Ber., 38, 856 (1905).

*References 12 through 27 are cited in Appendix I.

Preceding page blank

16. Fuson, R. C., and McKeever, C. H., "Organic Reactions," Vol. I, p. 63, Wiley, New York (1942).

17. Darzens, G., and Levy, A., Compt. Rend., 202, 73 (1936).

18. Badger, G. M., Cook, J. W., and Crosbie, G. W., J. Chem. Soc., 1432 (1947).

19. Grummitt, O., and Buck, A., "Organic Synthesis," Coll. Vol. III, p. 195, Wiley, New York (1955).

20. Feigl, F., "Chemistry of Specific, Selective, and Sensitive Reactions," Academic Press, Inc., New York, p. 305 (1949).

21. Noller, C. R., "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, p. 857 (1957).

22. Stamberg, K., Chem. Prumysl, 12, 686 (1962); C. A. 58, 12731f.

23. Gregor, H. P., Belle, J., and Marcus, R. A., J. Amer. Chem. Soc., 77, 2713 (1955).

24. Myers, G. E., and Boyd, G. E., J. Phys. Chem., 60, 521 (1956).

25. Soldano, B. A., and Larson, Q. V., J. Amer. Chem. Soc., 77, 1331 (1955).

26. Marinsky, J. A., J. Phys. Chem., 71, 1572 (1967).

27. Whitmore, F. C., "Organic Chemistry," Van Nostrand, New York (1943).

28. Dow Chemical Co., "DOWEX: Ion Exchange," Dow Chemical Co., Midland, Michigan (1959).

APPENDIX I

SYNTHETIC APPROACHES

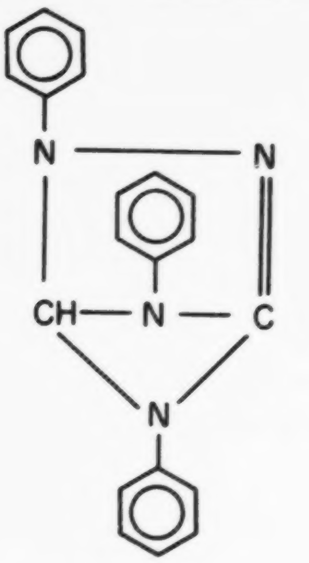
In this appendix, we give details of the reasoning which led to our choice of the particular synthetic approach used. Many of the possible avenues of investigation were not followed, but we present these ideas in the hope that they will be of interest to future workers in the field.

Present practice in the field of commercial, ion-exchange resins is based on the use of modified, styrene-divinylbenzene copolymers. This structural system is not only the least expensive, but it also has long life in use since the framework is formed by addition polymerization of nonoxygenated monomers.

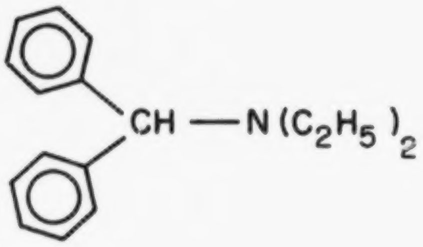
Initial study of a new system of ion-exchange resins for any given ion logically turns to modification of the proven, styrene-divinylbenzene copolymers. These may be sulfonated, nitrated, or chloromethylated to yield useful resins as they are, or they may undergo subsequent reactions. This system is well established; the bead or suspension polymerization technique is ideally suited to provide rheologically desirable particles. Any approach to a new resin should incorporate as much of this known technology as possible. Yet, for the task at hand, one must not limit oneself to proven approaches.

A highly desirable objective in the synthesis of a nitrate-specific, ion-exchange resin is the preparation of a resin containing functional groups known to retain nitrate ion. These structures are shown below:

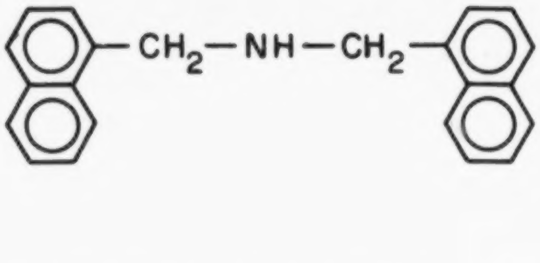
Nitron (1, 4-Diphenyl-endanilo-dihydrotriazol):



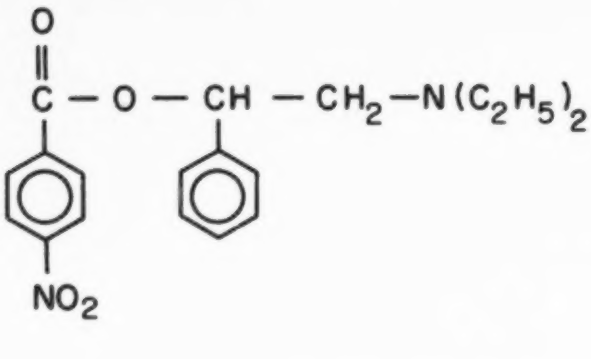
N, N-diethylbenzohydrylamine:



Di-(1-naphthylmethyl)-amine:



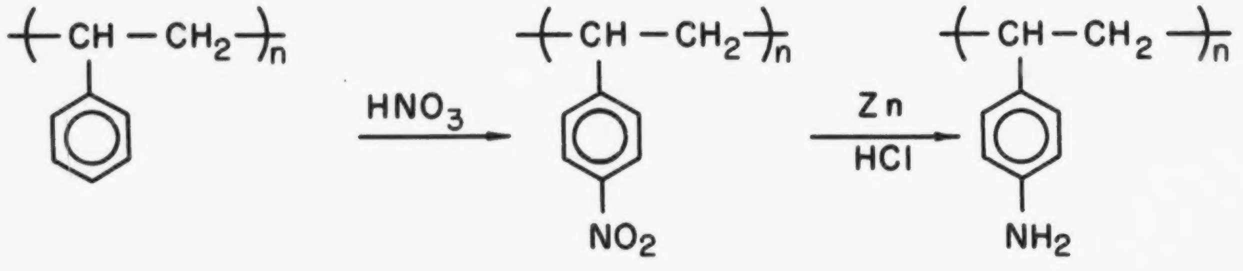
α-Phenyl-β -diethylaminoethyl-p-nitro-benzoate:

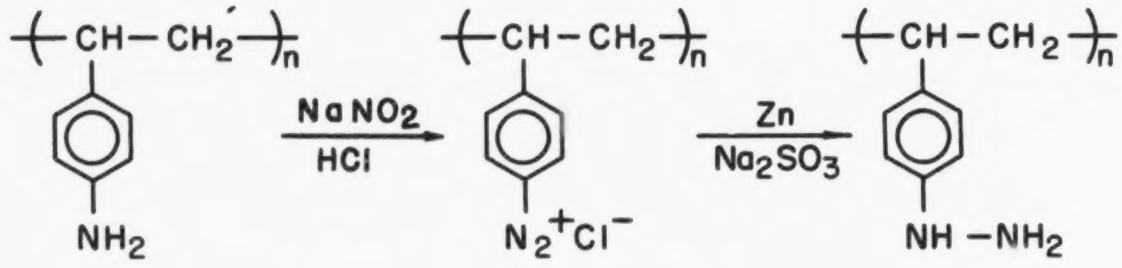


Procedures for incorporating the first and third structures into ion-exchange resins are proposed. Several governing factors, such as yields, the size of a group which may penetrate a resin matrix, and reaction and control of resin particle size, may only be determined by experiment.

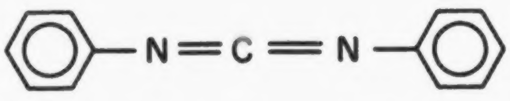
Nitron-Based Resin Synthesis: A first approach to synthesis of a nitrate-specific resin incorporating the "nitron" moiety follows.

Polystyrene is nitrated and reduced to the monoamino compound according to the method of A. Skogskeid.[8] The amino group is diazotized and reduced to the hydrazino group by sodium sulfite and zinc.[14] These reactions are set out below:

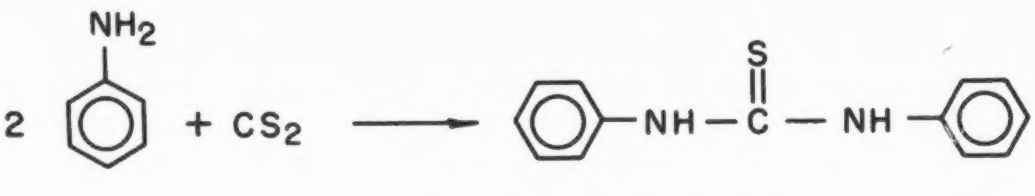

CH
CH2
n
HNO3
NO2
Zn
HCl
NH2


CH
CH2
n
NH2
NaNO2
HCl
N2+Cl−
Zn
Na2SO3
NH −NH2

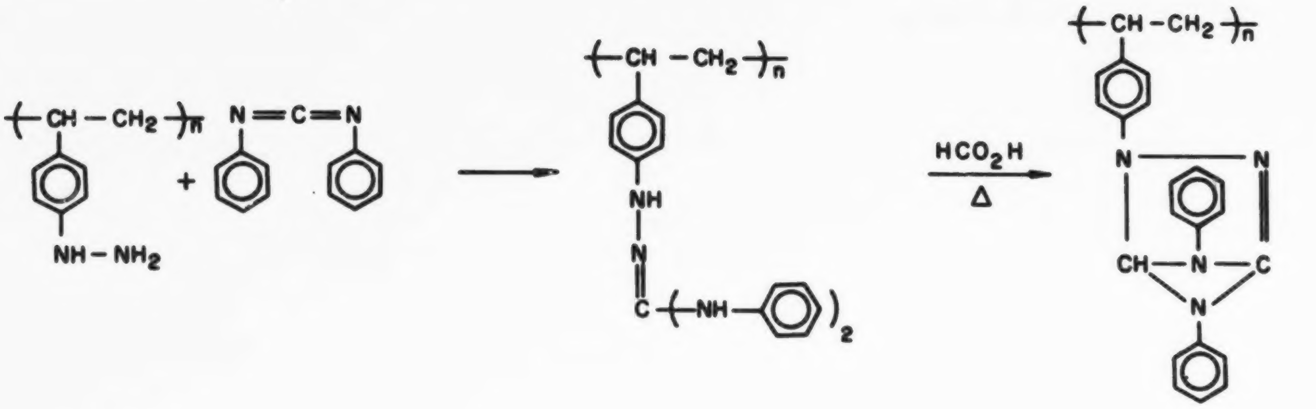
Phenylcarbodiimide:



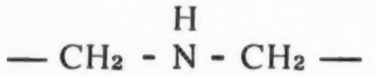
is available from the same reaction sequence used by Busch in his original synthesis of nitron.[15] Aniline and carbon disulfide react readily to give thiocarbanilide:[14]


NH2
2
+ CS2
S
NH
C
NH

which, upon treatment with lead oxide (PbO), yields phenylcarbodiimide. Busch added phenylhydrazine (in our case, a solution of the hydrazino polystyrene) to a benzene solution of carbodiimide to form the intermediate, triphenylaminoguanidine. This, in turn, is heated with 90% formic acid to yield nitron.



Di-(1-naphthylmethyl)-amine-Based Resin Synthesis: Another nitrate-ion retaining group:



$$-CH_2-\overset{H}{N}-CH_2-$$

is found in di-(1-naphthylmethyl)-amine. When fixed in a solid-state resin, the optimum sequence of (aromatic ring)-CH_2-NH-CH_2-phenyl (or naphthyl) that will retain nitrate must be determined. Several synthetic approaches available include:

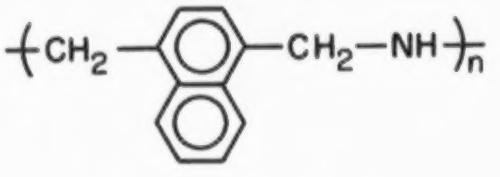
1. A vinylnaphthalene-polymer base can be (a) chloromethylated and treated with 1-naphthylmethylamine; or (b) the base can be chloromethylated, treated with ammonia, then treated with 1-chloromethylnaphthalene.

2. Polyvinylnaphthalene can be cross-linked by divinylbenzene, then treated as above.

3. A vinylnaphthalene-styrene-divinylbenzene terpolymer base can be treated as in 1. In 1(a) and 2, groups such as phenyl-CH_2-NH-CH_2-naphthyl may result. It is known, however, that the naphthalene nucleus chloromethylates more rapidly than the substituted phenyl ring.[16] Also, Darzens and Levy[17] report 90% yields for the chloromethylation of naphthalene. Other polymers containing the di-(1-naphthylmethyl)-amine grouping are readily prepared. Considerable care must be exercised in most chloromethylation reactions to limit substitution to one group; di-chloromethylation can readily occur, for example.

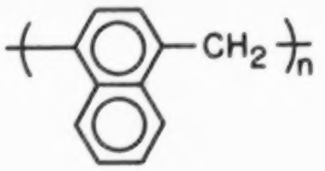
4. A resin based on methylaminomethylnaphthalene can be synthe-

sized. For example, 1,4-bis-chloromethylnaphthalene was prepared by Badger, Cook, and Crosbie,[18] who made appropriate modifications of the known techniques. Treatment with NH_3 could lead to a structure such as:

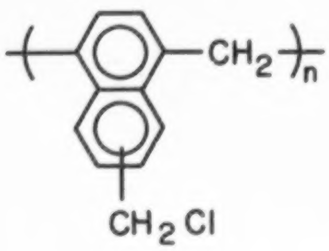


This polymethylnaphthylmethylamine could provide useful, nitrate-specific, anion-exchange resin properties.

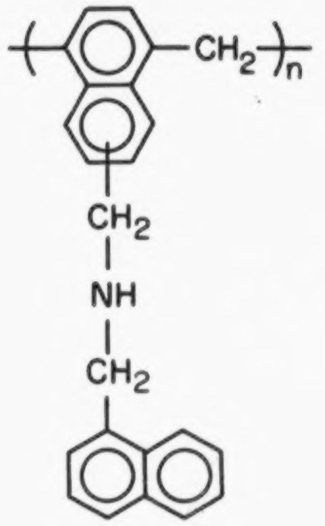
5. Polynaphthylmethyl-resin is another approach. Grummitt and Buck, in their preparation of methylnaphthalene,[19] note that if all catalyst is not removed before distillation, resinification occurs. We would allow resinification to take place, add more chloromethyl groups, and then proceed as in 1(a) or (b), above. The expected product of the first resinification is:



On further chloromethylation, this would give:



and, in turn, after 1(a) or (b), above:



This synthesis, if technically useful, could form the basis of a commercially feasible process for resin manufacture. The procedure would involve (1) chloromethylation of naphthalene using 1.5 to 1.7 mol ($-CH_2Cl$) per mole naphthalene, (2) allowing resinification to take place, (3) addition of ammonia, and (4) addition of 1-chloromethylnaphthalene. Since all of the raw materials are commercially available and cost less than $0.10/lb, an inexpensive, anion-exchange resin would result.

1-Naphthylmethylamine-Resin Synthesis: This resin turned out to be of the greatest interest to the present program. We have already discussed its properties to a considerable extent in the first part of this report.

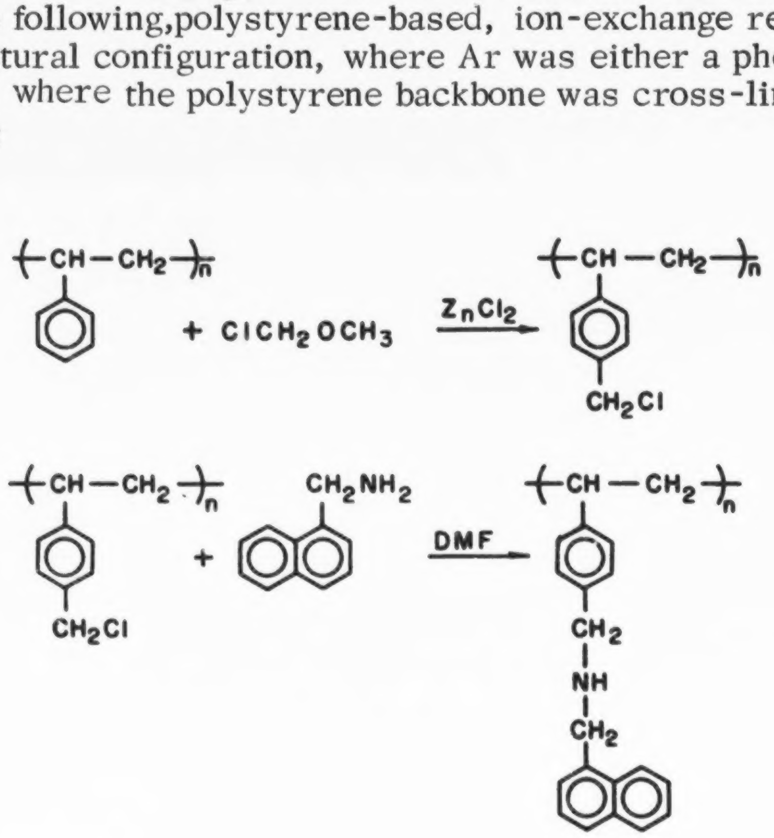
Of the known nitrogen bases which form insoluble nitrate salts, there is no structural similarity other than large molecular volume.[20] In fact, the structure of one of these, nitron, is probably incorrect since the assigned structure violates Bredt's rule[21] regarding bridgehead double bonds. The recent work of Hutton, Salam, and Stephen[12] on the use of N-substituted 1- or 2-naphthylmethylamines as specific nitrate-ion precipitants has yielded the only information on structural variations within a given class of precipitants.

These workers found that the molecule must possess the 1-naphthylmethylaminomethyl ($1\text{-}C_{10}H_7 \cdot CH_2 \cdot NH \cdot CH_2$ —) configuration for the insoluble nitrates to be formed. When the second methyl is substituted with a phenyl group, the sensitivity of the precipitation is quite high, even higher than the commonly used reagent, "nitron." These authors' study of N-benzyl 1- or 2-naphthylmethylamines as nitrate-ion precipitants showed that the steric configuration of the aromatic nucleus has only a slight effect on the solubilities of their corresponding nitrates. Therefore, the structural configuration, $\mathrm{Ar{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}Ar}$ (where Ar is an aromatic moiety), may offer the most promising configuration to be introduced into an ion-exchange resin.

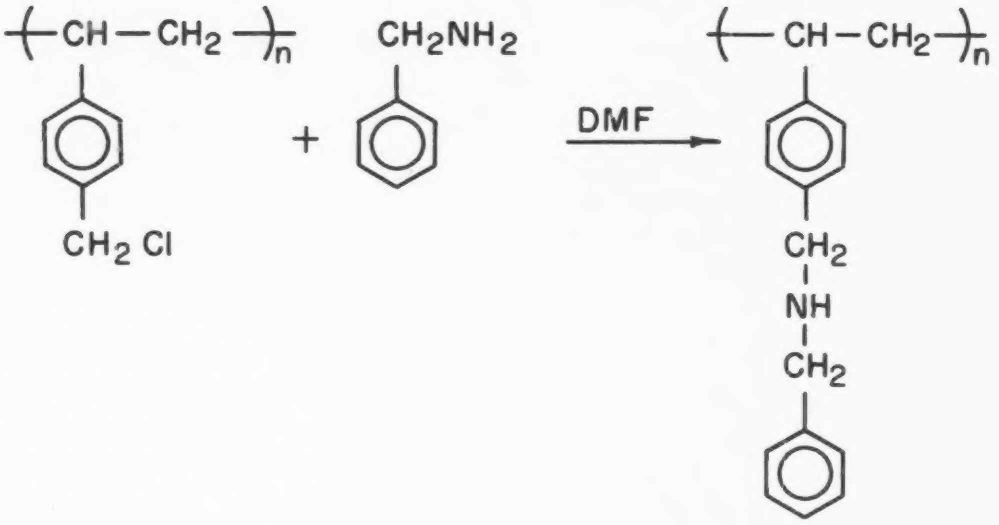
Several studies[22-25] have been conducted to determine the reasons for the selectivity of certain ion-exchange resins. The most useful and important observation from these studies was that the amount of cross-linking in styrene-based polymers had a pronounced effect on the selectivity and capacity of such ion-exchange resins. For example, as the amount of divinylbenzene in polystyrene sulfonate was increased from 0% to 12%, the selectivity of the resin for one ion over another also increased for a given pair of cations. This effect had also been predicted theoretically with some accuracy.[26]

In the present study, if the resin chosen for synthesis shows some selectivity for nitrate ion, the selectivity might be improved by incorporating the ion-specific reagent into divinylbenzene-styrene copolymers containing optimum amounts of divinylbenzene. Thus, another useful parameter (namely, the degree of cross-linking) is available for the successful synthesis of a nitrate-specific, ion-exchange resin.

We have shown in this study that incorporation of the structural configuration, $\mathrm{Ar{\cdot}CH_2{\cdot}NH{\cdot}CH_2}$—, into a polystyrene-based polymer yields a nitrate-specific, ion-exchange resin. To this end, we have successfully synthesized the following,polystyrene-based, ion-exchange resins containing the above structural configuration, where Ar was either a phenyl or 1-naphthyl group and where the polystyrene backbone was cross-linked with 2% divinylbenzene:



or,



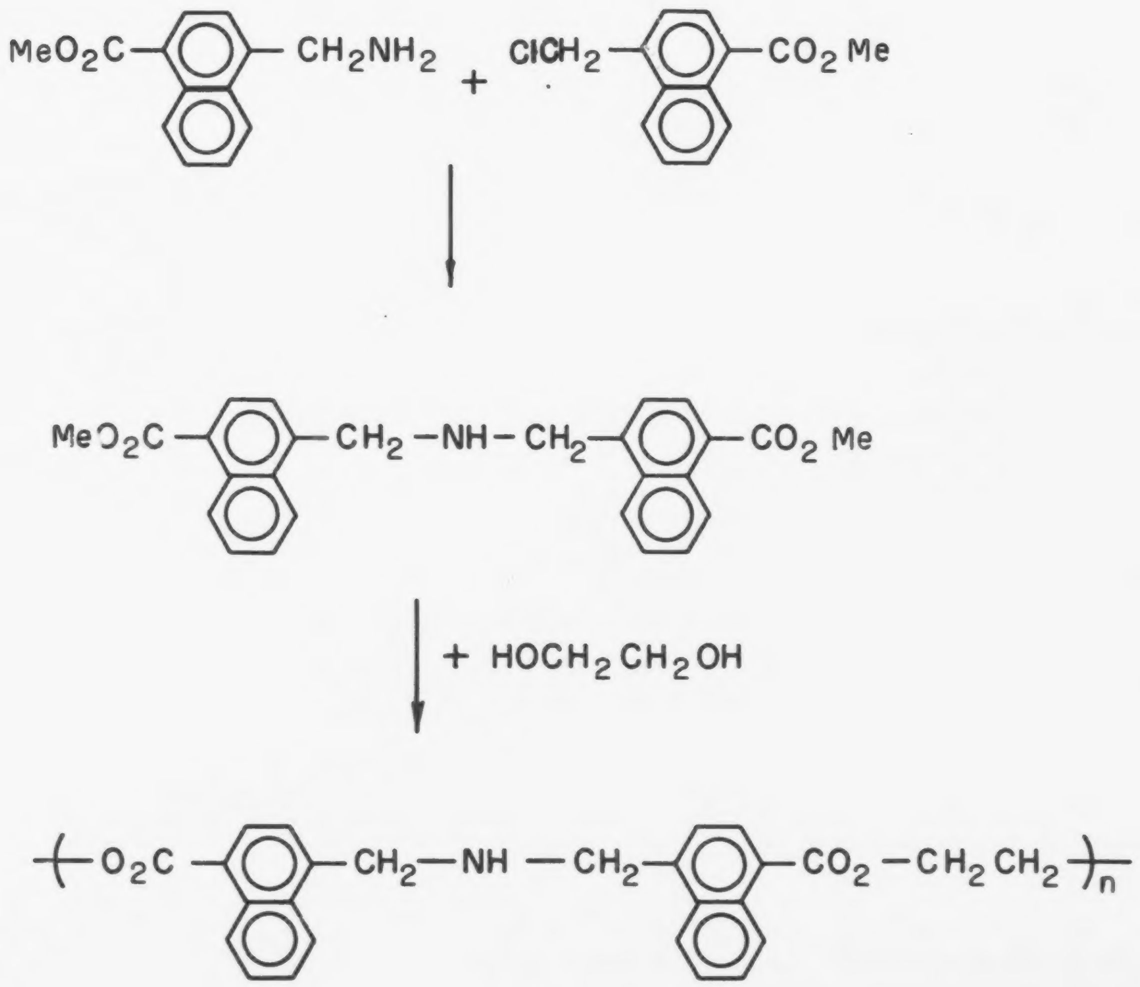
We have found that both of these resins exchange nitrate ion for chloride ion. The outlines of the synthetic procedures and ion-exchange determinations are given in Appendix II.

Other Nitrate-Specific, Resin Syntheses: The configuration of the salinogen-base monomers suggests that other compounds may exist that are simpler to form and more specific for nitrate than any of those previously tried. Since a compound of this type is to be attached to polystyrene or other resins to provide the necessary water-insolubility of the reagent and its products, it may be possible to use an amine that does not itself possess a highly insoluble nitrate. This simpler amine would need to possess only the necessary bond angles and spacings for preferred formation of the nitrate salt, rather than the salts of other common anions.

Thus, the choice is not limited to the gravimetrically useful, salinogen bases which must combine a high degree of selectivity with insolubility. Absorption spectroscopy could be utilized to distinguish between amines having soluble but nonionized nitrates and those with salts more loosely bonded. Visible and ultraviolet absorption measurements should allow selection of candidate reagents for incorporation into ion-exchange resins which would then offer the optimum combination of high selectivity and exchange capacity.

Alternatively, chloromethylated polystyrene may be treated with ammonia, then with benzyl chloride. Any tendency of chloromethylated polystyrene (a substituted benzyl chloride) to form unwanted amine byproducts may be reduced by using acetamide in place of ammonia.[27] This reaction would be followed, in turn, by treatment with benzyl chloride. These reactions are run commercially in preparing the benzyltrimethylammonium chlorides.

Although polystyrene is an inexpensive, readily available, ion-exchange-resin base, other resins may provide synthesis advantages over polystyrene. For example, polyester resins could be prepared by condensation of a carboxylic-acid-ester-substituted dinaphthylmethylamine with ethylene glycol. First, the substituted dinaphthylmethylamine would be made by reaction of aminomethyl naphthoic acid ester with a chloromethylnaphthoic acid ester. Copolymerization with ethylene glycol could then follow, as shown:



The properties of such a linear polymer would be expected to be quite different from those of polystyrene.

We have noted, above, that increasing the amount of cross-linking improves resin selectivity. In October, 1968, a considerable amount of time was spent on preparing resins with a larger amount of cross-linking (6%) than before (2%). The selectivity of these resins for nitrate ion over sulfate ion was determined. The selectivity of certain resins for nitrate ion over phosphate ion was also studied. The procedure for the resin synthesis and ion-exchange determinations, plus the experimental results obtained, are outlined in Appendix II.

Evaluation of Ion-Exchange Resins: In addition to evaluating resin efficiency in the removal of nitrate ion, several techniques and analytical devices can be used to identify the intermediates and products of the resin-synthesis routes previously described. These involve established, organic, analytical chemical techniques, with the necessary modifications and refinements for application to resin intermediates. Infrared and ultraviolet absorption spectroscopy can also be used, as well as nuclear magnetic resonance methods.

In the "polynitron" sequence, for example:

1. Nitration of styrene is followed by nitrogen analysis and by the infrared absorption of the aromatic nitro group.

2. Reduction to the aminopolystyrene is determined by nitrogen analysis, the formation of salts, and/or acidimetric titration.

3. The next stop, diazotization, is itself proof of the aromatic, primary amino structure. Skogskeid[8] reports that the diazotized compounds couple readily with beta-naphthol, resulting in characteristic dyes (usually red). This is a further means of identifying the diazotized product.

4. The conversion of the diazonium salt to the hydrazino compound is determined by consumption of the reductant, the reducing properties of the hydrazino group, and by its many reactions with carbonyl compounds to form hydrazones.

5. The nitrogen content of a polystyrene containing one hydrazino ($-NH-NH_2$) group on each benzene ring is 23.2%, but drops to 16.5% in the idealized structure in which there is a nitron group for each benzene ring. Also, analytical advantage may be taken of the perchlorate-binding capacity of nitron. Both the number of available sites and the extent of reaction can be followed by a chloride determination. It may also be desirable to develop standardized absorption spectra which have quantitative meaning in terms of

functional group content.

Following synthesis and identification of the anion-exchange resins, as previously described, performance evaluations must be carried out to determine their nitrate-adsorption capacity, their specificity in the presence of other anions such as chloride, sulfate, and phosphate, and their exchange-rate characteristics. Initially, these evaluations would be performed batchwise by agitating the resin beads (in either the hydroxide, carbonate, or chloride form) with a nitrate solution of known composition and at a level comparable to that expected in the effluent water. These tests, with water analyses performed by well-established,colorimetric methods for the ions involved, allow determination of the resin capacity and its specificity relative to interfering ions.

Resins that appeared to have desirable characteristics from the initial batch-screening tests were evaluated further in a laboratory, fixed-bed, ion-exchange column. Total elution curves were determined for each of the anions present to demonstrate nitrate selectivity and total capacity.

In this work, syntheses offering the possibility of eventual manufacture of ion-exchange resins at an attractively low cost were emphasized. Dr. Henry A. Hill of the Riverside Research Laboratory, Inc., Haverhill, Massachusetts, who has a broad background in commercial production of synthetic organic chemicals, was retained as a consultant during this program to ensure its sound economic orientation and to suggest alternative routes that might provide the same desired result at a lower cost.

APPENDIX II

DETAILED NOTES ON EXPERIMENTAL WORK

This section is a chronological account of our research on this program, and includes some specific experiments which were unsuccessful and certain research concepts which did not prove fruitful. Additional experimental data on the results summarized in the preceding sections are also presented here since these data may prove useful to future workers.

SYNTHETIC WORK (JULY 1968 — NOVEMBER 1968)

Based on the concepts discussed in Appendix I, a series of resins which incorporated the structural configuration, $Ar \cdot CH_2 \cdot NH \cdot CH_2$ —, into a polystyrene-based polymer was synthesized. The procedures used in this synthetic work are described below.

Preparation of 2%-Divinylbenzene-Styrene Copolymer: Into a 2-l, three-necked, resin flask equipped with thermometer, mechanical stirrer, and reflux condenser, were placed 650 ml of water and 50 ml of a 2%, aqueous, magnesium silicate solution. Agitation was begun, and a solution containing 98.00 g of styrene, 2.00 g of divinylbenzene, and 1.64 g of ethylstyrene (in which 1.00 g of benzoyl peroxide was dissolved) was added to the contents of the flask. The stirred mixture was then heated to 90 °C and held there for 1.5 hr, after which the mixture was heated to reflux for an additional hour. The reaction mixture was cooled to room temperature; then, the solid copolymer beads were separated by filtration, washed four times with water, air-dried, and finally oven-dried at 125 °C to constant weight.

Preparation of Chloromethylated Copolymer: Thirty grams of the copolymer beads, prepared above, was placed in a 1-l, four-necked, resin flask equipped with thermometer, mechanical stirrer, and reflux condenser. Sixty grams of freshly distilled, monochlorodimethyl ether was added, and the mixture was allowed to stand at room temperature for 15 min, during which time the copolymer beads swelled. The mixture was then diluted with 69 ml of petroleum ether (bp 30° to 60 °C), and agitation was begun. The reaction mixture was cooled to 0 °C by means of an ice-salt bath, and at this point, small portions of 18.3 g of anhydrous, powdered, aluminum chloride were added over a period of 1 hr. After this, the mixture was stirred at 0 °C for 2 hr. Ice water (500 ml) was slowly added in order to decompose the excess aluminum chloride and chloromethyl ether. The resulting mixture was stirred for 30 min and then filtered. The light-brown-colored beads were washed eight times with water, air-dried, and finally oven-dried at

125 °C to yield 41 g of chloromethylated copolymer.

Preparation of N-benzylaminomethyl Cross-Linked Polystyrene: Thirty grams of chloromethylated copolymer beads was suspended in 125 ml of dimethylformamide (DMF) in an Erlenmeyer flask and allowed to stand for 1 hr. The suspension was warmed to 35° to 40 °C, and 43.6 ml of benzylamine was added slowly with stirring. The mixture was then stirred for 2 hr at 50° to 60 °C, cooled, and filtered under vacuum. The light-brown-colored beads were washed with water, air-dried, and finally oven-dried at 125 °C to yield 32 g of ion-exchange resin.

Preparation of 1-Aminomethylnaphthalene: To 53.1 g of 1-chloromethylnaphthalene and 42.0 g of hexamethylenetetramine (HMTA), in a round-bottomed flask, was added 49.5 g of sodium iodide in 420 ml of hot ethanol. This mixture was allowed to stand for 2 hr at 50 °C. After this period, 55 ml of concentrated hydrochloric acid was added, and the mixture was subjected to distillation to remove the aqueous alcohol. The remaining residue was made alkaline with 3M sodium hydroxide solution, and then this aqueous mixture was extracted with diethyl ether. The ether extract was dried over anhydrous sodium sulfate, and the ether was removed by flask evaporation. The residue was then vacuum distilled to give 16 g of 1-aminomethylnaphthalene (bp 93° to 100 °C/0.4 mm Hg).

Preparation of N-(1-naphthylmethyl) -aminomethyl Cross-Linked Polystyrene: A suspension of 7.6 g of chloromethylated copolymer in 45 ml of dimethylformamide was prepared in an Erlenmeyer flask and allowed to stand for 1 hr. After this time, 15.0 g of 1-aminomethylnaphthalene was added slowly with stirring; then, the mixture was heated to 50° to 60 °C and stirred for 2 hr. The mixture was cooled and filtered, and the light-brown-colored beads were washed once with methanol and then with water. These beads were air-dried and finally oven-dried at 125 °C to yield 10 g of ion-exchange resin.

Preparation of 6%-Divinylbenzene-Styrene Copolymers: Into a 2-l, three-necked, resin flask equipped with thermometer, mechanical stirrer, and reflux condenser, were placed 500 ml of H_2O, 2 g of polyvinyl alcohol (PVA), and 0.4 g of Rexyn 201 ion-exchange resin. After the PVA had dissolved, a solution of 94.0 g of styrene, 10.9 g of 55% DVB-45% ethylvinylbenzene mixture, and 1.0 g of 2,2'-azobis(2-methylpropionitrile) was added, with rapid stirring, at 40 °C. The reaction mixture was heated at 80° to 90 °C for 1.5 hr, then at reflux for an additional 1.5 hr. The reaction mixture was cooled to room temperature; then, the solid beads and granules of copolymer were separated by filtration, washed with water, air-dried, and finally vacuum-oven-dried at 125 °C to constant weight.

Preparation of the Ion-Exchange Column: The preparation of the ion-exchange column was identical for all resins; the procedure for N-benzylaminomethyl cross-linked polystyrene ("benzyl resin") will be described. Before the benzyl resin was placed in the column, it was washed with 10% sulfuric acid and then washed free of acid with water. The swelled resin beads were placed in the column, and 100 ml of 0.01N HCl was passed through. The resin was again washed with water until no further chloride ion precipitated with 0.1M silver nitrate solution. The column was treated with 25 ml of 0.01M potassium nitrate solution, and after 10 ml of this solution had passed through, a test for chloride ion with silver nitrate solution was positive. This indicated that the resin exchanged chloride ion for nitrate ion. Similar results were obtained when N-(1-naphthylmethyl) -aminomethyl cross-linked polystyrene resin was used.

ION-EXCHANGE STUDIES (SEPTEMBER 1968)

For each of the three resins studied, the ion-exchange column was prepared as outlined above for the benzyl resin. Thus, 4 g of dry benzyl-resin beads was swelled in 50 ml of 5% HCl for 1 hr and then transferred to a column where it was washed with 25 ml of 0.1M HCl. The appropriate salt solutions were then passed through the column.

N-benzylaminomethyl Cross-Linked Polystyrene (Benzyl Resin): To determine the capacity of the benzyl resin, a 0.1M potassium nitrate (KNO_3) solution was passed through a column, prepared as above, and the effluent was tested for chloride and nitrate ions with aqueous silver nitrate and an acetic acid solution of Nitron, respectively. After 90 ml of the KNO_3 solution (0.009 g-eq) had passed through the column, nitrate ion as well as chloride ion were detected. Another 30 ml of KNO_3 solution (0.003 g-eq) was required before chloride ion was absent. Therefore, the capacity of the column for nitrate ion was 0.012 g-eq. Based on one exchange site per styrene unit, the theoretical exchange capacity for the column was 0.0155 g-eq.

To determine the selectivity of the benzyl resin for nitrate ion over sulfate ion, a column (identical to that above) was set up, and an aqueous solution containing 0.05M KNO_3 and 0.05M sodium sulfate (Na_2SO_4) was passed through. The effluent was tested at 10-ml intervals for chloride, nitrate, and sulfate ions with aqueous silver nitrate, an acetic acid solution of Nitron, and aqueous barium chloride, respectively. After 60 ml (0.006 g-eq of sulfate ion, plus 0.003 g-eq of nitrate ion) of the NO_3^-/SO_4^{2-} solution had passed through the column, sulfate ion as well as chloride ion were detected. Another 60 ml (0.003 g-eq of nitrate ion) was required before nitrate ion was detected, and an additional 30 ml (0.0015 g-eq of nitrate ion) was required before chloride ion was absent. It can be concluded that the benzyl resin is more selective toward nitrate ion than toward sulfate ion, and that the total capacity of the column was 0.0135 g-eq. Based on the total capacity of the column, the selectivity for nitrate ion was 0.0075/0.0135 = 0.555, and for sulfate ion was 0.006/0.0135 = 0.445. The selectivity ratio was 1.25:1.

N-(4-chlorobenzyl)-aminomethyl Cross-Linked Polystyrene (4-Chlorobenzyl Resin): A column containing the 4-chlorobenzyl resin was prepared, and its selectivity for nitrate ion over sulfate ion was determined, as just described above. Sulfate ion and chloride ion were detected after 40 ml (0.004 g-eq of sulfate ion, plus 0.002 g-eq of nitrate ion) of effluent had been collected. Another 70 ml (0.0035 g-eq of nitrate ion) of NO_3^-/SO_4^{2-} was passed through before nitrate ion was detected, and an additional 50 ml (0.0025 g-eq of nitrate ion) of solution was required before chloride ion was absent. Again, we may conclude that the 4-chlorobenzyl resin is more selective for nitrate ion than sulfate ion. The total capacity was 0.012 g-eq. The selectivity for nitrate ion was 0.008/0.012 = 0.666, and for sulfate ion was 0.004/0.012 = 0.333. The selectivity ratio was 2:1.

N-(1-naphthylmethyl)-aminomethyl Cross-Linked Polystyrene (Naphthylmethyl Resin): In a manner similar to that described above, a column containing the naphthylmethyl resin was prepared, and its selectivity for nitrate ion over sulfate ion was determined. After 20 ml (0.002 g-eq of sulfate ion, plus 0.001 g-eq of nitrate ion) of the NO_3^-/SO_4^{2-} solution had passed through the column, sulfate ion and chloride ion were detected. Another 60 ml (0.003 g-eq of nitrate ion) was collected before nitrate ion was detected, and an additional 10 ml (0.0005 g-eq of nitrate ion) was eluted before chloride ion was absent. Again, we may conclude that the naphthylmethyl resin is more selective for nitrate ion than sulfate ion. The total capacity of the resin was 0.0065 g-eq. The selectivity for nitrate ion was 0.0045/0.0065 = 0.69, and for sulfate ion was 0.002/0.0065 = 0.31. The selectivity ratio was 69:31 = 2.2:1.

ION-EXCHANGE STUDIES (OCTOBER 1968)

For each of the resins studied, the ion-exchange column was prepared as outlined above.

N-benzylaminomethyl 6%-Cross-Linked Polystyrene (6% Benzyl Resin): The determination of selectivity for nitrate ion over sulfate ion, for resins containing 6% cross-linking, was as follows. A column was set up, as described above, and an aqueous solution containing 0.005M potassium nitrate and 0.005M sodium sulfate was passed through. The effluent was tested at 10-ml intervals for chloride, nitrate, and sulfate ions with aqueous silver nitrate, an acetic acid solution of Nitron, and aqueous barium chloride, respectively. After 410 ml (0.0041 g-eq of sulfate ion, plus 0.0021 g-eq of nitrate ion) of the NO_3^-/SO_4^{2-} solution had passed through the column, sulfate ion as well as chloride ion were detected. Another 210 ml (0.0011 g-eq of nitrate ion) was required before nitrate ion was detected, and an additional 100 ml (0.0005 g-eq of nitrate ion) was required before chloride ion was absent. Based on the total capacity of the column, the selectivity of the resin for nitrate ion was 0.0037/0.0078 = 0.475, and for sulfate ion was 0.0041/0.0078 = 0.525. The selectivity ratio was 1.1:1. This value is the opposite of that obtained for the same resin with 2% cross-linking, and it must be concluded that this resin is more selective for sulfate ion than for nitrate ion.

N-(4-chlorobenzyl)-aminomethyl 6%-Cross-Linked Polystyrene (6% 4-Chlorobenzyl Resin): In a manner similar to that described above, a column containing the 6% 4-chlorobenzyl resin was prepared, and its selectivity for nitrate ion over sulfate ion was determined. After 280 ml (0.0028 g-eq of sulfate ion, plus 0.0014 g-eq of nitrate ion) of the NO_3^-/SO_4^{2-} solution had passed through the column, sulfate ion and chloride ion were detected. Another 200 ml (0.0010 g-eq of nitrate ion) of solution was collected before nitrate ion was detected, and an additional 130 ml (0.0007 g-eq of nitrate ion) was eluted before chloride ion was absent. The total capacity was found to be 0.0059 g-eq. The selectivity for nitrate ion was 0.0031/0.0059 = 0.580, and for sulfate ion was 0.0028/0.0059 = 0.470. The selectivity ratio was 1.2:1. This value is less than that (2:1) obtained for the same resin with 2% cross-linking.

N-benzylaminomethyl 2%-Cross-Linked Polystyrene (2% Benzyl Resin): The selectivity for nitrate ion over phosphate ion was also determined for two resins. A column containing the 2% benzyl resin was prepared as described above, and an aqueous solution of 0.025M KNO_3 and 0.025M disodium hydrogen phosphate was passed through. The presence of phosphate was determined using an aqueous ammonium molybdate solution, followed by reduction with stannous chloride. After 10 ml (0.0005 g-eq of phosphate ion, plus 0.00025 g-eq of nitrate ion) of the nitrate-phosphate solution had passed through the column, phosphate as well as chloride ions were detected. Another 30 ml (0.00075 g-eq of the nitrate ion) of solution was passed through before nitrate was detected, and an additional 260 ml (0.0065 g-eq of nitrate ion) of solution was required before chloride ion was absent. The total capacity was found to be 0.008 g-eq. The selectivity for nitrate ion was 0.0075/0.008 = 0.940, and for phosphate ion was 0.0005/0.008 = 0.063. The selectivity ratio was 14.7:1.

N-(4-chlorobenzyl)-aminomethyl 2%-Cross-Linked Polystyrene (2% 4-Chlorobenzyl Resin): In a manner similar to that described above, a column containing the 2% 4-chlorobenzyl resin was prepared, and its selectivity for nitrate ion over phosphate ion was determined. Phosphate ion was detected in the first 10 ml (0.0005 g-eq of phosphate ion, plus

0.00025 g-eq of nitrate ion) of effluent. Another 20 ml (0.0005 g-eq of nitrate ion) was collected before nitrate ion was detected, and an additional 160 ml (0.004 g-eq of nitrate ion) was eluted before chloride ion was absent. The total capacity of the column was 0.00525 g-eq. The selectivity for nitrate ion was 0.00475/0.00525 = 0.905, and for phosphate ion was 0.0005/0.00525 = 0.095. The selectivity ratio was 9.52:1.

Comparing the results on selectivity for nitrate ion over sulfate ion, with changing percentages of cross-linking, we see that the resins containing 2% DVB are more selective than the resins containing 6% DVB. This is the opposite of what has been observed previously. Until more experimental work is carried out, no explanation is offered for this discrepancy. In the study of the selectivity for nitrate ion over phosphate ion, using resins with 2% cross-linking, it appeared that the resins investigated were more selective toward nitrate ion. However, these results are not conclusive since phosphate ion was detected almost immediately (i.e., there appeared to be very little exchange of phosphate ion for chloride ion).

SELECTIVITY ANALYSIS (NOVEMBER 1968)

Samples of 2%- and 6%-cross-linked N-benzylaminomethylstyrene (benzyl resin) were prepared. The wet capacities for the free-base form of the 2%- and 6%-cross-linked resins were 1.40 meq/ml and 0.70 meq/ml, respectively. The dry capacities of the benzyl resins in their hydrochloride form were 1.60 meq/g and 1.05 meq/g for the 2% and 6% materials, respectively.

The selectivity of the resins in their hydrochloride form for nitrate over chloride and sulfate ions was also determined from the selectivity relationship described in Eq. (2). For the 2%-cross-linked resin, $S(NO_3^-/Cl^-)$ was 4.1 and $S(SO_4^{2-}/Cl^-)$ was 1.2. For the 6%-cross-linked resin, $S(NO_3^-/Cl^-)$ was 5.9 and $S(SO_4^{2-}/Cl^-)$ was 2.0.

RESIN SYNTHESIS (DECEMBER 1968)

Extensive screening was initiated to obtain a nitrate-ion-specific, ion-exchange resin. To keep the results consistent, a sample of commercial cross-linked polystyrene was obtained. The sample consisted of a mixture of cross-linked polystyrenes containing 2%, 6%, and 8% divinylbenzene in equal proportions. This material was chloromethylated according to the procedure given above. Portions of the chloromethylated product were then reacted with several primary amines in dimethylformamide to yield weak-base, ion-exchange resins. The following amines were reacted: ethyl, isopropyl, benzyl, 4-chlorobenzyl, 4-methylbenzyl, and 1-naphthylmethyl.

In order to determine the amount of chloromethylation that had taken place, a sample of the chloromethylated material was reacted with trimethylamine. This ion-exchange material is identical with the commercial material, Dowex-1. The capacity of both resins was determined in an identical manner. The Dowex-1 resin had a capacity of 0.80 meq/ml, while our synthesized material had a capacity of 0.78 meq/ml. This is a good indication that our material had undergone the desired amount of chloromethylation.

RESIN CAPACITY (JANUARY 1969)

During this period 11 weak-base, ion-exchange resins were successfully prepared by reaction (in DMF) of the amines with a mixture containing equal amounts of 2%, 6% and 8%-divinylbenzene-cross-linked, chloromethylated polystyrene. The structure of each of these resins was:

Ⓟ — CH_2 — NH_2^+ — R Cl^-

where Ⓟ is cross-linked polystyrene, and R is an alkyl or aryl group.

The weak-base capacities of the resins listed in Table VI were determined in the following manner. A 4-g sample of the resin hydrochloride was placed in a 10-cm-i.d. column and washed with 5% sodium hydroxide solution until the effluent was chloride-ion free. The column was then rinsed with deionized water to a neutral pH. The sample was removed from the columns and divided into two approximately equal portions which were placed in graduated cyliners. The cylinders were vibrated until the resin had completely settled; then, the actual volume occupied by the resin was recorded. The samples were washed into 250-ml volumetric flasks. Exactly 50 ml of 1 N hydrochloric acid was added, and the contents diluted to the mark. The samples were allowed to equilibrate for at least 16 hr, with occasional shaking. After this period, two 25-ml aliquots were pipetted into 125-ml beakers, and each aliquot was titrated with 0.1N sodium hydroxide to a pH of 7. The wet-volume capacity for the free base was calculated from the following equation:

$$\frac{50 - (\text{ml } 0.1\text{N NaOH})}{\text{ml sample}} = \text{meq/ml}$$

Complete transfer of the samples allowed us to estimate the dry capacity by dividing the total capacity of the sample by the dry weight.

Table VI. Weak-Base Capacities of Synthesized Resins

Resin*	Wet Capacity, meq/ml	Dry Capacity, † meq/g
Isopropylamine	0.88	1.61
n-Butylamine	0.89	1.53
t-Butylamine	0.72	1.33
n-Hexylamine	0.22	0.38
Cyclohexylamine	0.29	0.50
n-Octylamine	0.35	0.58
Benzylamine	0.42	0.91
p-Methylbenzylamine	0.29	—
p-Chlorobenzylamine	0.16	0.26
N-Methylbenzylamine	0.23	0.40
1-Naphthylmethylamine	0.17	0.27
Rexyn 203	2.32	4.14

---

*The resin is listed according to the amine used for its formation by reaction with chloromethylated polymer.

†Estimated.

If the values of the capacities of synthesized resins (listed in Table VI) are compared with those of a commercial resin (Rexyn 203) of similar structure, it may be seen that the capacities of the synthesized resins are much lower than those of the commercial resin. Since the amount of chloromethylation had been determined, it was expected that the capacities would be much higher than those actually observed. Apparently, complete reaction between the amine and the chloromethylated polymer was not achieved.

To improve the capacity of the resins, we suggest that the amination reaction be carried out at higher temperatures. The amount of covalent chloride (i.e., the remaining free chloromethyl groups) can be determined, as a measure of completeness of this reaction, in the following manner. A weighed sample of the resin hydrochloride can be reacted with an aqueous, 30%, trimethylamine solution for 24 hr. The solution can then be carefully acidified with excess 5N nitric acid, and titrated potentiometrically with 0.1 N silver nitrate. This treatment will give individually the total, ionic, and covalent chloride contents. To verify our explanation, the covalent chloride content can be determined by subtracting the known, ionic, chloride content from the total chloride content.

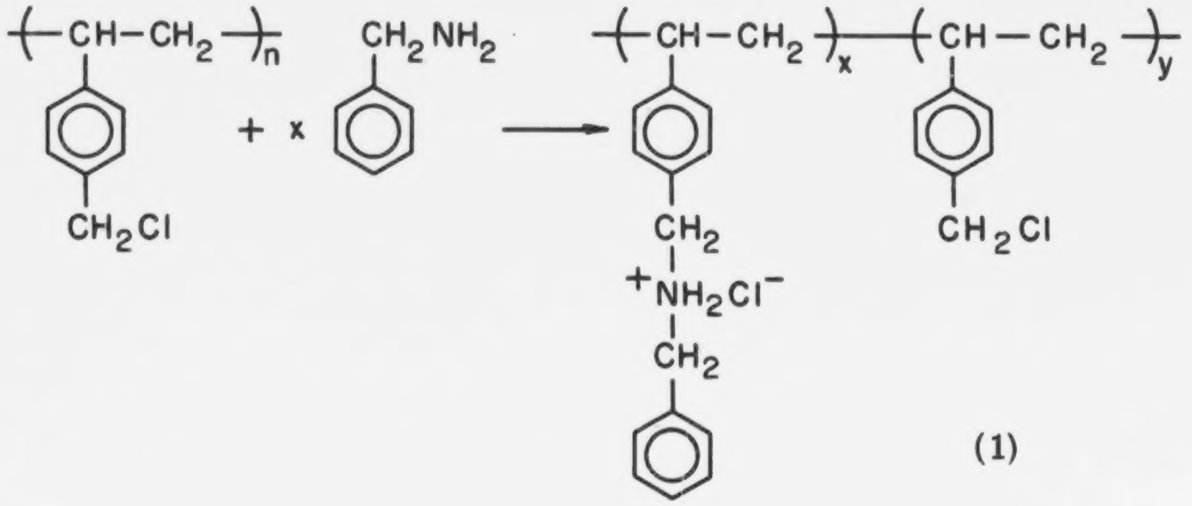
RESIN SYNTHESIS AND STRUCTURE DETERMINATION
(FEBRUARY 1969)

As discussed above, the observed low capacities of the synthetic resins were believed to arise from incomplete reaction between the chloromethylated copolymer and the amine. A method to test this explanation, based on a determination of the quantity of ionic and covalent chloride present after amination, was outlined and carried out. The results are discussed below.

Another batch of chloromethylated polystyrene was prepared, as described above. The total number of chloromethyl groups (or total potential capacity) was determined by reacting the chloromethylated copolymer with trimethylamine, followed by displacing the chloride ions by nitrate ions.

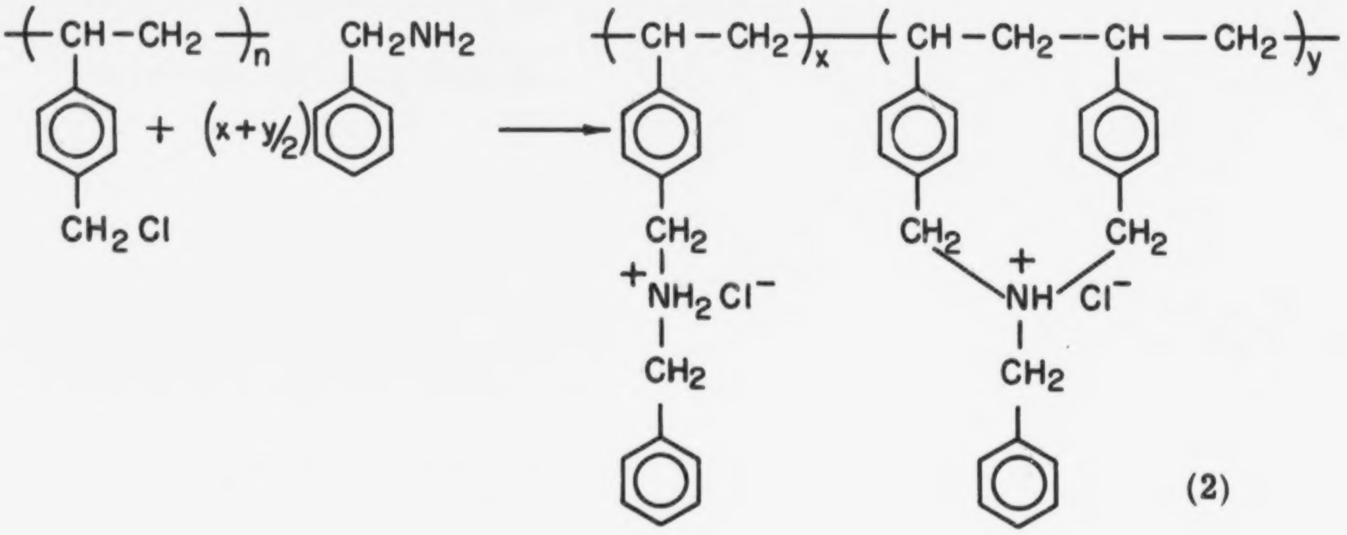
When the chloride ions were potentiometrically titrated with silver nitrate solution, it was determined that the resin contained 3.52 meq/g of ionic chloride (74.4% of the theoretical capacity). Because of the high reactivity of trimethylamine, it was assumed that complete reaction had occurred, and that the polystyrene had been 74.4% chloromethylated. This value represents the maximum percentage of theoretical capacity which could be obtained for any ion-exchange resin formed by aminating this sample of chloromethylated polystyrene. The value is necessary for comparison with the capacity value of the resin prepared by reacting benzylamine with the chloromethylated copolymer.

A sample of the same chloromethylated polystyrene was reacted with a twofold excess of benzylamine in refluxing benzene for 24 hr. The possible reactions are:



(1)

where x + y = n, or:



(2)

where x + y/2 = n.

Reaction (1) would be incomplete, and the product would contain unreacted chloromethyl groups (or covalent chloride), as well as ionic chloride, at the exchange sites. The ionic chloride was determined by displacement by nitrate ions, followed by potentiometric titration of chloride ion. The resin was found to contain 2.31 meq/g of ionic chloride; i.e., the capacity was 2.31 meq/g. The covalent chloride (or number of unreacted chloromethyl groups) was determined by reacting a sample of the incompletely benzylated material with trimethylamine. Exchange of the resin chloride ion for nitrate ion, followed by potentiometric titration, gave a value of 2.37 meq/g for the total chloride ion. Thus, within experimental error, there was no further reaction with trimethylamine. There were no unreacted chloromethyl groups, and reaction (1) was not the correct mechanism.

Although there appeared to be no free chloromethyl groups in the resin after reaction with benzylamine, the exchange capacity (2.31 meq/g) was considerably lower than that calculated [provided that chloromethyl sites were converted to ion-exchange sites on a one-to-one basis (3.02 meq/g)]. We concluded, therefore, that aminations carried out with benzylamine (and, probably, with other primary and secondary amines) may bring about cross-linking. This cross-linking was ascribed to reaction (2); that is, reaction of more than one chloromethyl group with the amine groups to form tertiary amines in the polymer. Reaction of the amine may occur with a second chloromethyl group in the same polymer chain, or in another polymer chain to provide cross-linking.

The significance of the conclusion is twofold. Not only is the capacity reduced by the formation of amine sites which are tertiary rather than secondary, but also the configuration

$$\textcircled{P} - \mathrm{CH_2} - \mathrm{NH} - \mathrm{CH_2R}$$

(where R is alkyl or aryl), which is expected to be nitrate-ion-selective (see above), is thereby destroyed. It is to be noted, however, that cross-linking can be prevented by lowering the rate of side reactions and enhancing the probability of the desired reaction. This can be done: (1) by a low concentration of polymer, and (2) by a large molar ratio of amine to chloromethyl groups.

CHLOROMETHYLATION OF POLYSTYRENE
(MARCH 1969)

Following discussions with Dr. H. Hill, we questioned whether the copolymer had undergone complete chloromethylation. Duplicate chlorine analyses were obtained for two, different, chloromethylated materials: samples 420-101 and 420-124. Sample 420-101 was found to contain 16.7% chlorine which was 71.5% of the theoretical value for one chloromethyl group per benzene ring of the copolymer. Sample 420-124 was found to contain 18.8% chlorine which was 80.5% of the theoretical value. These results agree with those reported in the literature; that is, complete chloromethylation is very rarely obtained, and most studies are carried out with material which is not completely chloromethylated.

The possibility was mentioned, in our discussion with Dr. Hill, that the method we were using to determine the amount of chloromethylation (as described above) did not yield conclusive results. However, we were able to prove that our method does give conclusive results. Samples of the two chloromethylated materials were reacted with trimethylamine in refluxing, 20%, aqueous dioxane for 48 hr, and the ionic chloride was determined (as described above). Sample 420-101 was found to contain 3.11 meq/g of chloride ion. This corresponded to 65.8% of the theoretical value (for the trimethylammonium derivative) of 4.73 meq/g, based on one chloromethyl group per benzene ring. This is to be compared with the chlorine-analysis value of 71.5%. Sample 420-124 contained 3.29 meq/g of chloride ion which was 69.5% of the theoretical value (compare this with the chlorine-analysis value of 80.5%). The results of the two methods are reasonably close, thus justifying our method using trimethylamine. It should also be noted that the trimethylamine values are probably as realistic as can be expected since complete amination is rarely achieved.

SELECTIVITY OF RESINS (FEBRUARY — MAY 1969)

There is a simple method for determining the nitrate-ion selectivity of a resin. For a resin to bind nitrate ion effectively (and selectively), the equilibrium constant, K, for the following reaction:

$$\textcircled{P}-CH_2-NH-R + HNO_3 \rightleftharpoons P-CH_2-\overset{+}{N}H_2-RNO_3^- \tag{3}$$

must be large. Let us choose a reference resin that is known to be selective for nitrate ion over chloride ion, and measure its K as defined above. Then, let us assume, as a criterion of nitrate-ion selectivity, that the K of another resin is (or, must be) ten times our standard K. We have chosen the commercial resin, Rexyn 203, as our reference. If another resin meets the above criterion, it will be evaluated further. The advantage of this method is that only nitrate-ion concentrations need be determined.

Because the resins are usually obtained in the hydrochloride form, we have modified Eq. (3) as follows:

$$\begin{aligned}\textcircled{P}^+-CH_2-\overset{+}{N}H_2-R\,Cl^- + NO_3^- &\rightleftharpoons \\ &\textcircled{P}^+-CH_2-\overset{+}{N}H_2-RNO_3^- + Cl^-\end{aligned} \tag{4}$$

The equilibrium constant for this reaction represents the selectivity of the resin for nitrate ion over chloride ion, as described above. As a criterion for a practical resin, the selectivity coefficient, S(NO_3^-/Cl^-), must be at least ten times greater than that of commercial resins, Rexyn 203 and Duolite A7.

We determined S(NO_3^-/Cl^-), for Rexyn 203 and Duolite A7, by equilibrating 1-g samples of the resin with 0.053M nitric acid. Since we are dealing with univalent ions, [RNO_3] and [Cl^-] must be equal and correspond to the difference between the initial and final nitrate-ion concentrations, [R Cl] must correspond to the initial [R Cl] concentration (i.e., the capacity of the resin), minus the difference between initial and final nitrate-ion concentration. Measurement of the resin capacities and nitrate-ion concentrations before and after equilibration yielded an S(NO_3^-/Cl^-) value of 4.7 for Rexyn 203, and a value of 3.8 for Duolite A7.

Selectivity could not be determined in this way for most of the resins synthesized earlier because of the extensive formation of tertiary amine groups. In order to obtain ion-exchange resins with only secondary-amine exchange sites, stringently controlled reaction conditions for the amination reaction must be followed. These conditions are: (1) low concentration of chloromethylated copolymer, and (2) a high molar ratio of amine to chloromethyl groups. Amination of chloromethylated copolymer, sample 420-101, was carried out in dioxane with a copolymer concentration in the range of 5×10^{-2} M and an amine-to-chloromethyl-group ratio of 20:1. The capacity, and therefore the amount of amination, was determined as described above.

Resins from the amination reaction with butyl-, benzyl-, and 1-naphthylmethylamines have been prepared. The capacities were 2.67, 2.25, and 1.71 meq/g, respectively. Taking into consideration that sample 420-101 was only 71.5% chloromethylated, these capacities correspond to 84.0%, 81.5%, and 74.0% of the theoretical, active-site yield, respectively. These capacities seem realistic when compared to the "control yield" from resins obtained by reaction with trimethylamine. We therefore believe that the resins prepared above contain predominately secondary, amine-exchange sites.

The selectivity coefficients determined for the above resins were 1.4, 2.7, and 26 for the n-butyl, benzyl-, and 1-naphthylmethyl resins, respectively. It should be noted that the value for the 1-naphthylmethyl resin can be in error by as much as 50% because of the conditions under which the exchange was carried out and the limitation of the analytical method. If we compare the above selectivities with those for Rexyn 203 (4.7) and Duolite A7 (3.8), we see that only the value of the 1-naphthylmethyl resin is significantly larger. This observation does offer a promise of success for obtaining a nitrate-ion-specific, ion-exchange resin.

Our caution in reporting the results for the 1-naphthylmethyl resin is based upon the possible errors which are inherent in selectivity calculations for high-selectivity resins. The experiment is carried out by treating the resin, in the hydrochloride form, with a known concentration of nitrate ion at pH 1.46. After suitable equilibration, the concentration of Cl^- in solution, $[\mathrm{Cl}^-]_{\mathrm{final}}$, is determined. The initial concentration of resin in the hydrochloride form, $[\textcircled{P}\,\mathrm{Cl}]_{\mathrm{initial}}$, is the previously determined capacity of the resin. The following calculations may then be made:

$$[\textcircled{P}\,\mathrm{Cl}]_{\mathrm{final}} = [\textcircled{P}\,\mathrm{Cl}]_{\mathrm{initial}} - [\mathrm{Cl}^-]_{\mathrm{final}}$$

$$[\textcircled{P}\,\mathrm{NO_3}]_{\mathrm{final}} = [\mathrm{Cl}^-]_{\mathrm{final}}$$

$$[\mathrm{NO_3}^-]_{\mathrm{final}} = [\mathrm{NO_3}^-]_{\mathrm{initial}} - [\mathrm{Cl}^-]_{\mathrm{final}}{}^{*}$$

$$S(\mathrm{NO_3}^-/\mathrm{Cl}^-) = \frac{[\textcircled{P}\,\mathrm{NO_3}]_{\mathrm{final}}[\mathrm{Cl}^-]_{\mathrm{final}}}{[\textcircled{P}\,\mathrm{Cl}]_{\mathrm{final}}[\mathrm{NO_3}^-]_{\mathrm{final}}}$$

For 0.91 g of 1-naphthylmethyl polystyrene, these values, in milliequivalents per 100 ml of solution, are:

$$[\textcircled{P}\,\mathrm{Cl}]_{\mathrm{final}} = 0.91\ (1.71) - 1.54 = 1.56 - 1.54 = 0.02$$

$$[\textcircled{P}\,\mathrm{NO_3}]_{\mathrm{final}} = 1.54$$

$$[\mathrm{NO_3}^-]_{\mathrm{final}} = 6.08 - 1.54 = 4.54$$

$$S(\mathrm{NO_3}^-/\mathrm{Cl}^-) = \frac{(1.54)\ (1.54)}{(0.02)\ (4.54)} = 26$$

Note that the value for $[\textcircled{P}\,\mathrm{Cl}]_{\mathrm{final}}$ is a small number derived from the difference between two large numbers, a situation inherently subject to large error. For example, if an error of only 1% were made in each of the measurements from which $[\textcircled{P}\,\mathrm{Cl}]_{\mathrm{final}}$ was determined, the calculated selectivity would be only 6.2.

In order to determine if the 1-naphthylmethyl resin was unique among polystyrene derivatives, a number of analogous, secondary amines were synthesized and tested. Table VII lists the capacities and selectivity coefficients for synthesized resins derived from ten different amines. The values for the commercial resins, Duolite A7 and Rexyn 203, are also included for comparison.

---

* Not accounting for any Cl^- removed by hydrolysis.

Table VII. Capacities and Selectivity Coefficients of Resins Derived From Chloromethylated Polystyrene and Selected Primary Amines

Primary Amine	Capacity, meq/g	Selectivity Coefficient, S
Benzyl	2.25	2.7
4-Chlorobenzyl	1.69	7.6
4-Methoxybenzyl	2.17	3.1
1-Naphthylmethyl	1.85	14.0
Isopropyl	2.59	7.0
n-Butyl	2.67	1.4
t-Butyl	2.51	7.0
n-Hexyl	0.98	6.4
Cyclohexyl	2.21	6.7
n-Octyl	1.07	4.3
Duolite A7	7.00	3.8
Rexyn 203	4.94	4.7

We see immediately that several of the resins have selectivities significantly larger than that of either Duolite A7 or Rexyn 203. However, one resin has a considerably higher value of S: the resin derived from 1-naphthylmethylamine. It may also be seen that the selectivity of the 1-naphthylmethyl resin is lower (14) than that reported previously (26). However, as discussed above, such differences may be inherent in the experimental determination of selectivity coefficients of high-selectivity resins.

It should be emphasized that, although the uncertainty of the higher selectivity coefficients remains, the comparative values are considered highly reliable. All determinations of selectivity coefficients in Table VII were carried out in an identical manner, by converting the resin to the hydrochloride form and then equilibrating it with a nitric acid solution of known concentration at pH = 1.5. Thus, the relative differences in selectivity coefficients among the resins tested in Table VII are indeed significant. Since Duolite A7 and Rexyn 203 are among the most selective commercial resins for nitrate ion over chloride ion, it appears that a significant improvement has been achieved with the 1-naphthylmethyl resin.

We attempted to establish a reliable value for the selectivity coefficient of the 1-naphthylmethyl resin. An experimental series, in which various, initial, chloride-ion and nitrate-ion concentrations in the equilibrating solutions were carefully chosen, was designed. The choice of the concentrations was based on the fact that the initial and final nitrate-ion and chloride-ion concentrations, and their respective differences, would be relatively insensitive to inherent experimental errors. The results of these calculations are presented in Table VIII.

Table VIII. Selectivity Coefficients for 1-Naphthylmethyl Resin at Various, Initial, Nitrate-Ion and Chloride-Ion Concentrations

$[NO_3^-]_{initial}$, M	$[Cl^-]_{initial}$, M	Selectivity Coefficient, S
0.031	0.1	8.7
0.032	0.05	7.5
0.017	0.05	12.5
0.057	0.05	14.0

We believe that the differences among the selectivity coefficients (S) reported in Table VIII are significant, and that S varies with the total ionic strength of the equilibrating solution. In studying the literature, we have observed the standard practice of reporting changes in S with variation of relative ion fraction at constant, total, ion concentration. Furthermore, the total ion concentration is almost invariably chosen so that the total number of ions in the equilibrating solution is equal to, or less than, the number of active exchange sites in the resin. We have been unable to locate examples in which the total ion strength was varied in batch equilibration experiments. We are reasonably certain, therefore, that the variations in Table VIII are not unusual. Furthermore, similar variations in S have been observed for Rexyn 203 in identical experiments.

Since the selectivity coefficients given above appear to depend on the ionic fractions of the equilibrating ions, and on the total concentration of the equilibrating ions, we redetermined the selectivity coefficients for Rexyn 203, Duolite A7, and the synthetic 1-naphthylmethyl resin in solutions in which the ionic fraction of nitrate ion (in meq) ranged from 0.32 to 0.75, and the total ionic concentration (in meq) was varied around a value of 1.90. The results of these selectivity coefficient measurements are presented in Table IX. The selectivity coefficients were determined in solutions of the indicated concentration, and equilibration was carried out for 3 days. The weights for the different resins were adjusted so that the total number of active sites (i.e., the capacity in meq) was approximately the same for each resin. It should be noted that the total ionic concentration exceeded the capacities of the resin by about 20%. This was due to the fact that the capacities of the resins were lower than expected after regeneration.

Table IX. Selectivity Coefficients for Rexyn 203, Duolite A7, and Synthetic 1-Naphthylmethyl Resin at Various Ionic Fractions

Total Equivalents*	Ionic Fraction of NO_3^- †	Selectivity Coefficient, S		
		Rexyn 203	Duolite A7	1-Naphthylmethyl Resin
1.89	0.323	2.5	1.8	8.2
1.93	0.435	2.4	1.9	9.7
1.94	0.542	2.2	1.8	9.6
1.93	0.637	2.1	2.0	7.8
1.93	0.745	1.9	1.7	8.2

---

* Total, initial concentration of nitrate and chloride ions (in meq) in the equilibration solutions.

† Ratio of concentration of nitrate ion to total ionic concentration (in meq) in the initial, equilibration solutions.

From the results in Table IX, we see that, as observed previously, the 1-naphthylmethyl resin has a significantly higher selectivity coefficient than either Rexyn 203 or Duolite A7. Also, there does not appear to be any significant variation in the selectivity coefficients with ionic ratios for the range studied. Differences in the selectivity coefficients for any given resin probably reflect the inherent errors in our determinations. Again, the variations in the selectivity coefficient for the 1-naphthylmethyl resin certainly seem to depend on the total ionic strength.

BREAKTHROUGH EXPERIMENTS (JUNE — AUGUST 1969)

During this period, we carried out breakthrough experiments on three resins: Rexyn 203, Duolite A7, and our synthetic 1-naphthylmethyl amine resin (1-NMA resin). The experimental procedure was as follows. Separate columns of each resin in the hydroxide (or free-base) form were made up with similar bed volumes (about 25 cc). The influent was an aqueous solution containing 350 mg/l (0.0056M) of nitrate ion and 990 mg/l (0.028M) of chloride ion at pH = 2. Each 25 ml of effluent was analyzed for nitrate ion, and every fifth, 25-ml sample was analyzed for chloride ion, and its pH was measured. Regeneration was accomplished by passing through 500 ml of 1M NaOH, followed by aqueous washing until the effluent was neutral.

The results, presented in Figs. 2 and 3, are for the second pass through each column. The data for the first pass were similar, but only 10 bed volumes of influent passed through before regeneration was initiated. The vertical lines in each graph represent points when the flow of effluent was stopped, and the columns were left standing overnight. From the known resin capacities and concentration of the influent, it should be noted that for Rexyn 203 and Duolite A7, insufficient solution has passed through at the 40-bed-volume mark to occupy completely all the active sites of the resin. However, for the synthetic resin, sufficient solution was added to saturate all the active sites.

Let us first consider Fig. 2 which shows the effluent, nitrate-ion concentration ratio as a function of throughput. For the 1-NMA resin, nitrate ion appears, at very low concentration, in the first 25 ml and remains at essentially the same level ($< 1 \times 10^{-4}$ M, < 10 mg/l) up to the passage of at least 40 bed volumes. In a similar experiment for Rexyn 203 and Duolite A7, nitrate ion appears in the first bed volume, but then it rapidly rises to a level of about 2.0×10^{-3} M (>100 mg/l) after the passage of only 3 bed volumes, and the nitrate-ion concentration remains essentially constant up to 20 bed volumes. The irregularities observed after these two columns stood overnight are discussed later. The significant result here is that the synthetic resin is much better at removing nitrate ion than either Rexyn 203 or Duolite A7. The 1-NMA resin reduced the influent nitrate-ion concentration by about 98%.

Two other results shown in Fig. 2 should be discussed. First, the initial, high pH of the effluents from Rexyn 203 and Duolite A7 probably corresponds to residual hydroxide ion being washed out. The later, effluent, pH values, which are close to neutrality, are expected since the influent is neutralized by the release of hydroxide as chloride and nitrate ions are taken up by the resin. Therefore, the effluent pH will equal the influent pH only after all the exchange sites have been neutralized. In the case of the

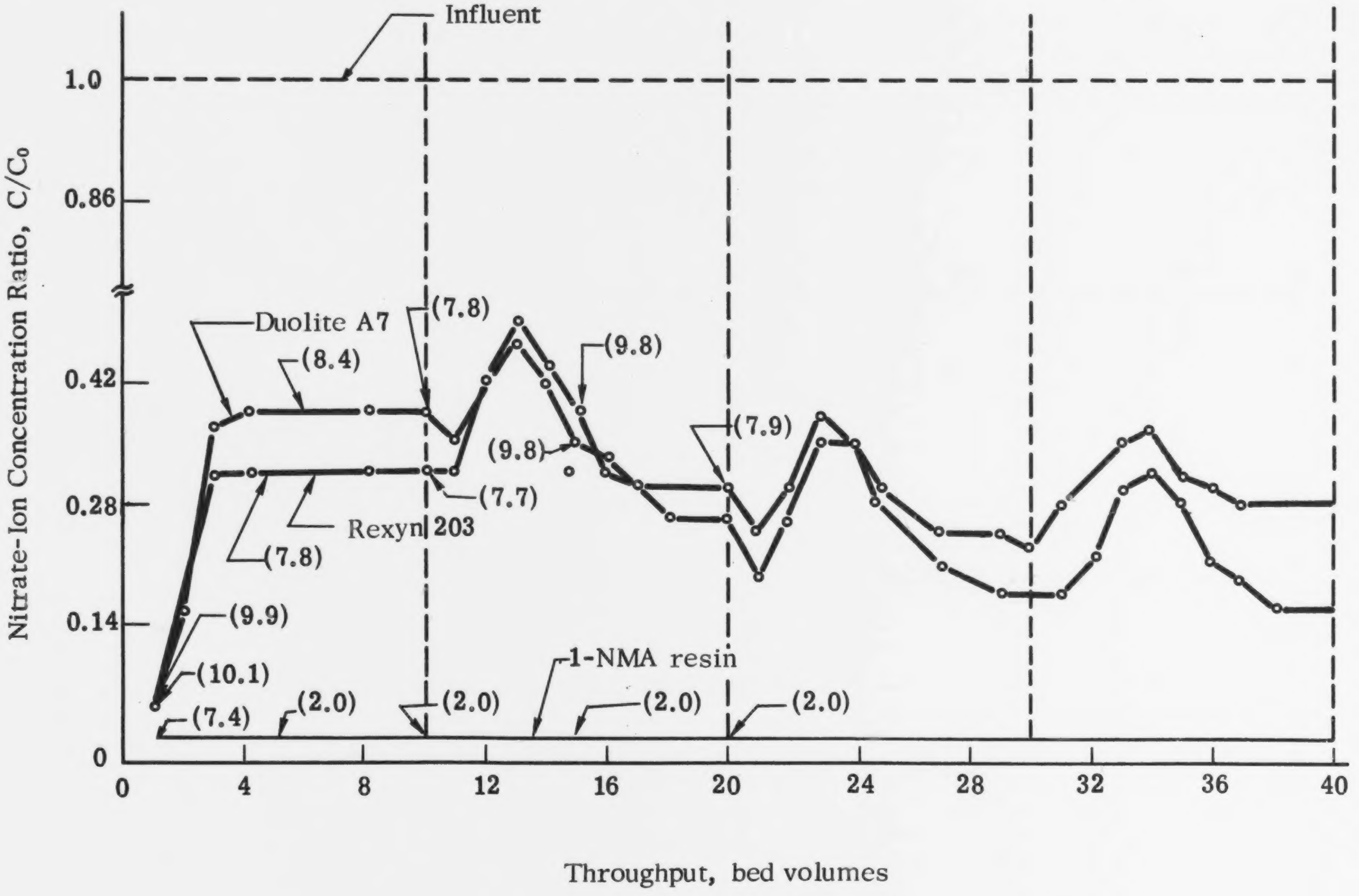


Fig. 2. Ratio of effluent to influent nitrate-ion concentration (C/C_0) as a function of throughput (numbers in parentheses are pH values; $C_0 = 5.6 \times 10^{-3}$M, one bed volume = 25 ml)

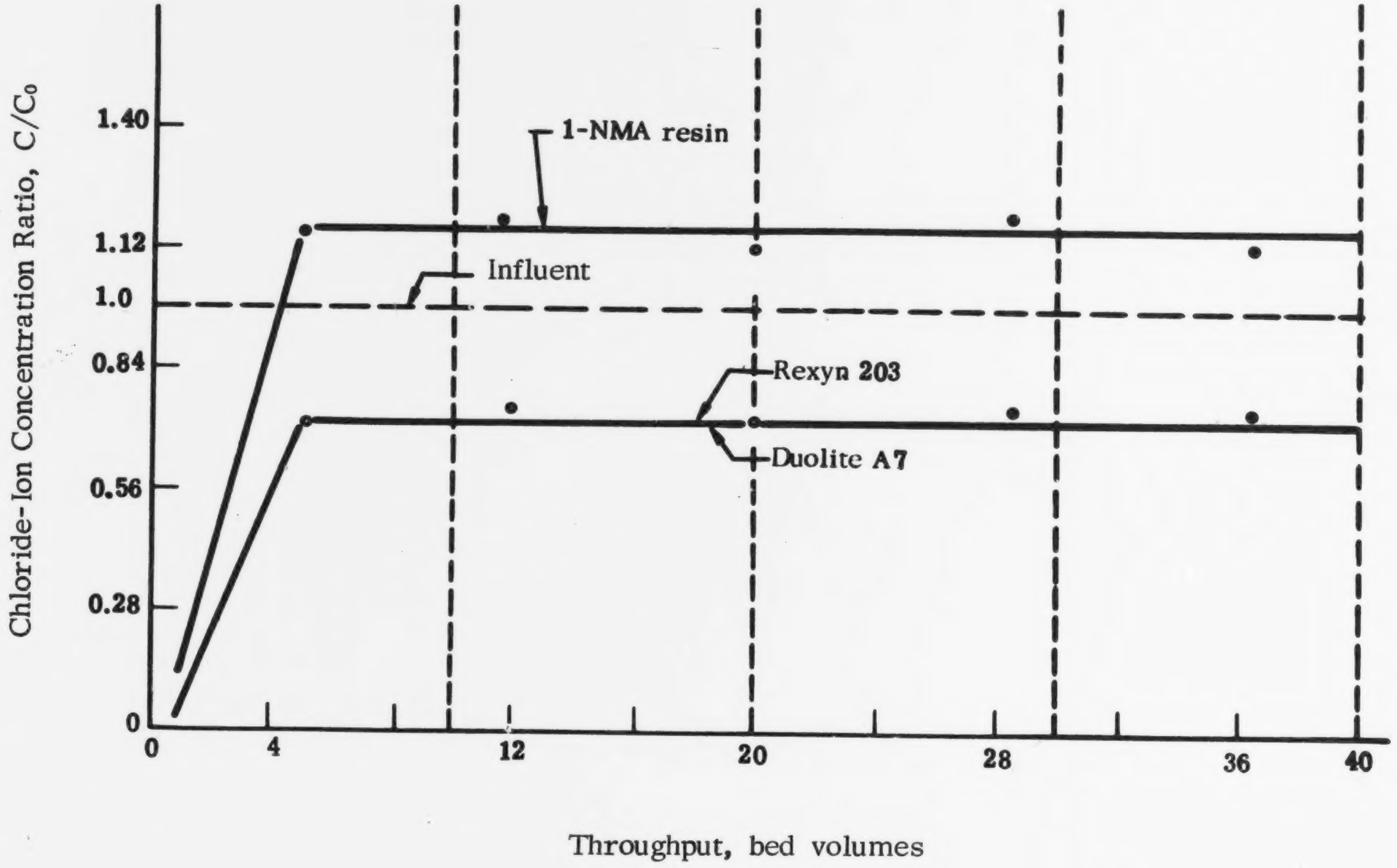


Fig. 3. Ratio of effluent to influent chloride-ion concentration (C/C_0) as a function of throughput ($C_0 = 2.8 \times 10^{-2}$ M, one bed volume = 25 ml)

1-NMA resin, in which the pH of the influent equals that of the effluent after the passage of 4 bed volumes, it appears that the resin is rapidly converted to the hydrochloride form. Therefore, after the passage of, at most, 4 bed volumes of influent, all the active sites are neutralized; then, the nitrate ion exchanges directly for chloride ion. Second, the irregularities in the nitrate-ion concentration, after the Rexyn 203 and Duolite A7 columns had stood overnight, are probably partially due to the inherent, experimental error in the nitrate-ion analyses, and partially to rate-controlled equilibration occurring on standing.

The effluent chloride-ion concentration is plotted as a function of effluent volume in Fig. 3. Within the first 25 ml (1 bed volume), chloride ion was detected in the effluent of each resin. The chloride-ion concentration then rose rapidly to a constant value after passage of 4 bed volumes in the case of Rexyn 203 and Duolite A7, and after 50 ml (2 bed volumes) in the case of the 1-NMA resin. It is to be noted that, for the 1-NMA resin, the effluent chloride-ion concentration is larger than the influent after passage of 2 bed volumes. This may correspond to the release of chloride ion as nitrate ion is selectively adsorbed. Thus, as influent passes through, more chloride ion is displaced (by nitrate ion) than is taken up (by hydroxide-ion exchange), and the effluent chloride-ion concentration becomes larger than that of the influent. In the case of Rexyn 203 and Duolite A7 on the other hand, the effluent chloride-ion concentration always remains below that of the influent. In fact, the constant, effluent, chloride-ion concentration (like the nitrate-ion concentration) can be explained by a kinetic effect; i.e., the ion-exchange rates are slow in comparison to the flow rate. Therefore, the effluent concentration remains constant until all the active sites reach equilibrium. At this point, there should be another, rapid rise in the chloride-ion and nitrate-ion concentrations for Rexyn 203 and Duolite A7. However, for the 1-NMA resin, the chloride-ion concentration will gradually drop to the same value as the influent.

To summarize: it has been observed that the 1-NMA resin removes nitrate ion very effectively (effluent concentration < 10 mg/l, 98% removal) in comparison with Rexyn 203 or Duolite A7. Furthermore, the ion-exchange rates for each resin appear to be very slow. Finally, in the case of the 1-NMA resin, the high, effluent, chloride-ion concentration is caused by exchange with nitrate ion.

We conducted our next breakthrough experiments with the same three resins in their hydroxide (free-base) form. The influent was an aqueous solution containing 350 mg/l (5.6×10^{-3} M) of nitrate ion and 990 mg/l (2.8×10^{-2} M) of chloride ion at pH = 2. The flow rate was 0.5 gal./min/cu ft. The physical properties of each column are presented in Table X. Nitrate-ion analyses were made with a nitrate-ion-specific electrode, and chloride-ion analyses were made either with a chloride-ion-specific electrode or by potentiometric titration.

Table X. Physical Properties of Resin Columns

Resin	Total Capacity, meq*	Height, cm	Ratio of Height to Diameter
1-NMA	18	8	4
Rexyn 203	30	8	4
Duolite A7	50	8	4

---

* Calculated from capacity in meq/g.

Figs. 4, 5, and 6 show the ratio of effluent concentration to influent concentration (C/C_0) as a function of the number of bed volumes of effluent for the 1-NMA resin, Rexyn 203, and Duolite A7, respectively.

Let us first consider the case of the 1-NMA resin. No appreciable nitrate ion appears in the effluent until 40 bed volumes has passed through the column, but the effluent chloride-ion concentration equals that of the influent after the passage of only 4 bed volumes. The effluent chloride-ion concentration then exceeds that of the influent for the next 66 bed volumes. Only after the passage of 70 bed volumes, does the effluent concentration equal that of the influent. We also found that the effluent pH equaled the influent after the passage of only 4 bed volumes. From these observations, a detailed analysis is possible.

Since the influent concentration is 0.0056M in nitrate ion and 0.028M in chloride ion, passage of 70 bed volumes corresponds to an input of 10 meq of nitrate ion and 49 meq of chloride ion; i.e., a total input of 59 meq. From the effluent analyses, we found a total of 54.5 meq of chloride ion and 2 meq of nitrate ion; i.e., a total output of 56.5 meq. Comparing the input and output values, we find that the 1-NMA resin retained 8 meq of nitrate ion, but gave up 5.5 meq of chloride ion.

It can be calculated, from Fig. 4, that the resin took up 1.5 meq of chloride ion from the first 4 bed volumes, but, subsequently, 7.0 meq was released, so that an excess of 5.5 meq of chloride ion appeared in the total effluent. Therefore, we must conclude that the "regenerated" resin initially was not entirely in its free-base form, but contained at least 5.5 meq of chloride ion. Furthermore, after the first 4 bed volumes of throughput, the amount of excess chloride ion per bed volume appearing in the effluent corresponded to the amount of nitrate ion taken up per bed volume. That is, it appears likely that exchange of nitrate ion for chloride ion occurred. This is also substantiated by the fact that the effluent

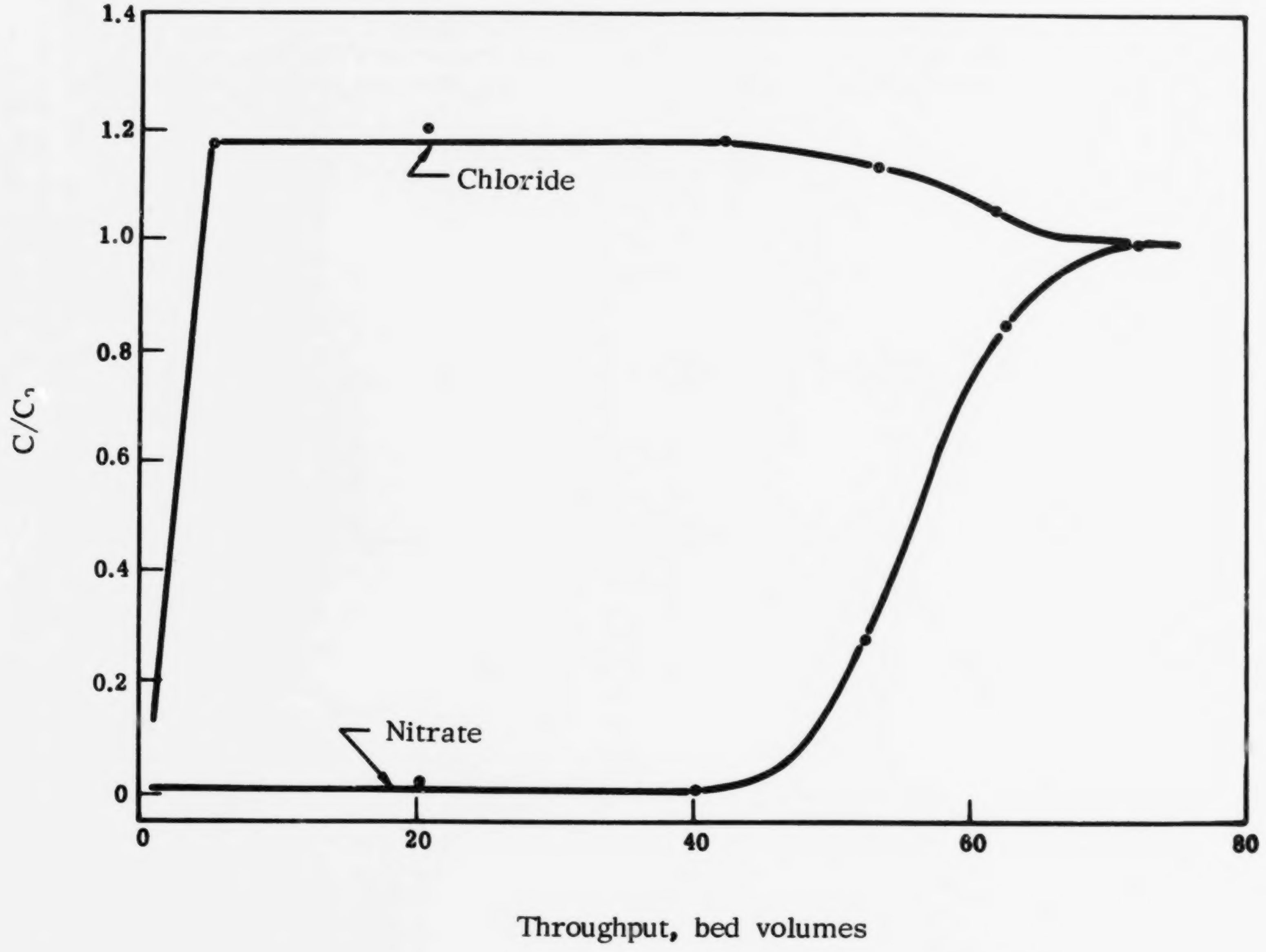


Fig. 4. Ratio of effluent concentration to influent concentration, C/C_0, as a function of throughput (in bed volumes) for the 1-NMA resin (influent contains 0.0056M nitrate ion and 0.028M chloride ion)

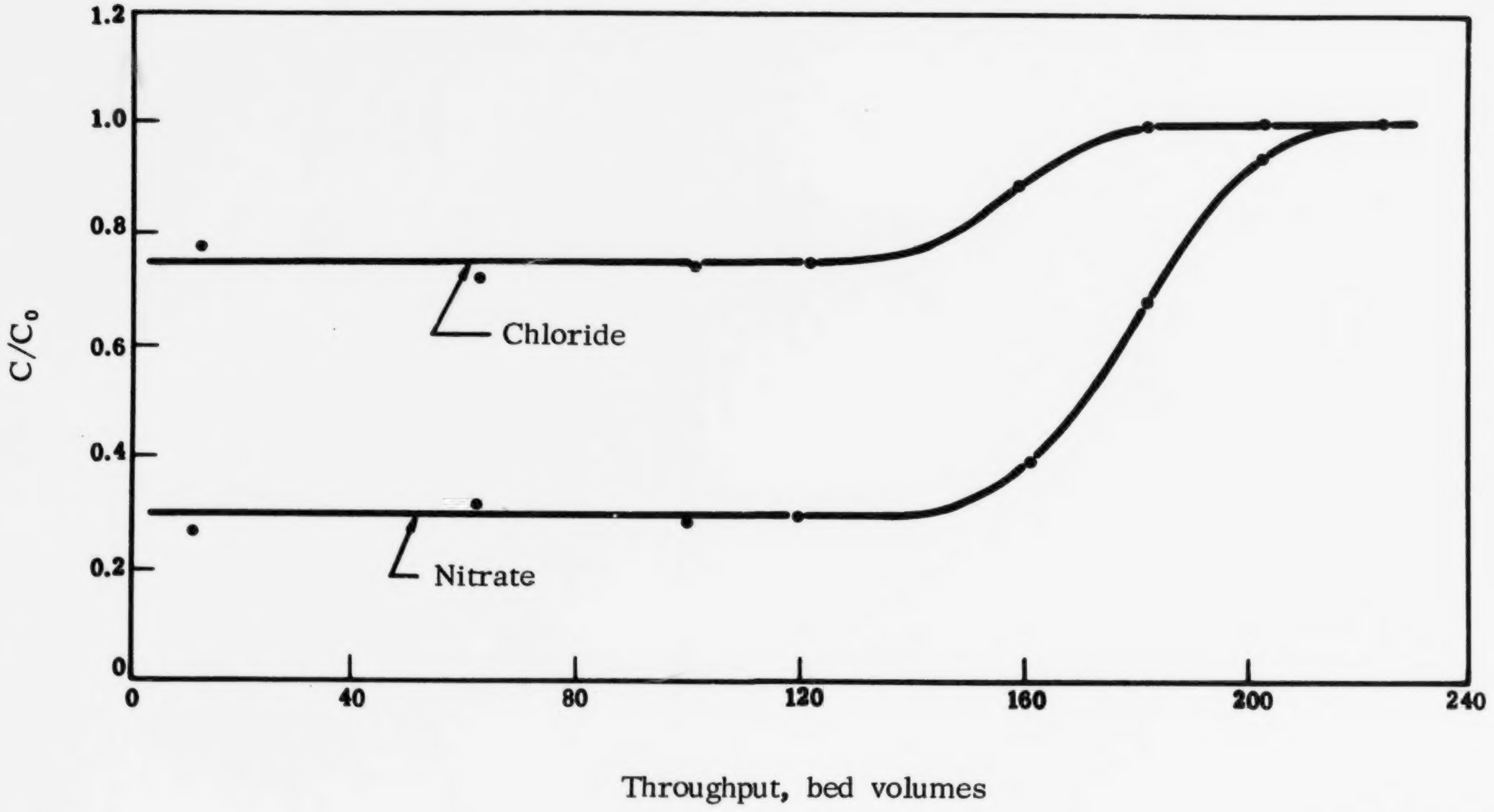


Fig. 5. Ratio of effluent concentration to influent concentration, C/C_0, as a function of throughput (in bed volumes) for Rexyn 203 (influent contains 0.0056M nitrate ion and 0.028M chloride ion)

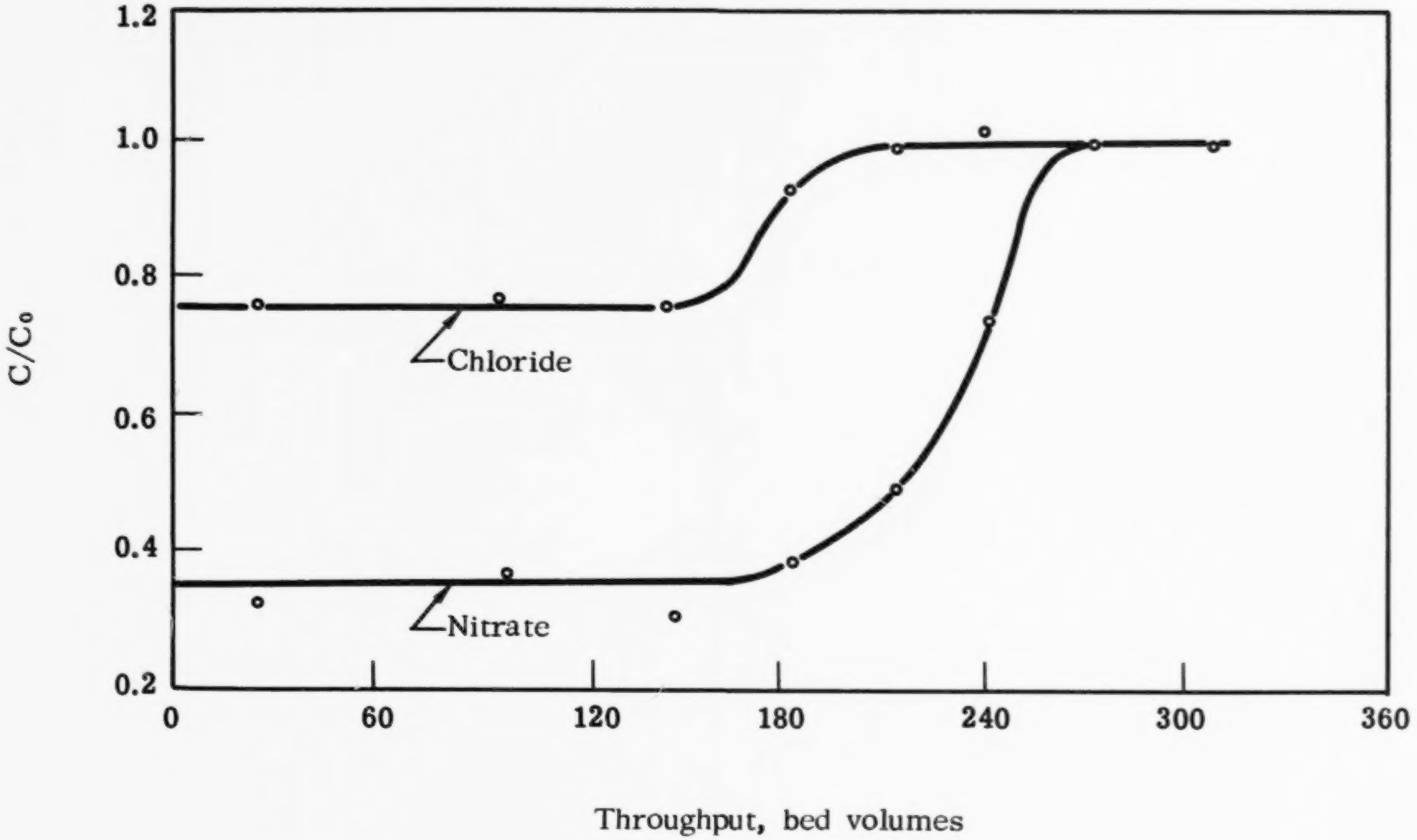


Fig. 6. Ratio of effluent concentration to influent concentration, C/C_0, as a function of throughput (in bed volumes) for Duolite A7 (influent contains 0.0056M nitrate ion and 0.028M chloride ion)

pH was equal to that of the influent in this region, and that the resin must be completely in the ammonium form.

The results for Rexyn 203 and Duolite A7 are very similar to one another, but they are quite different from those for the 1-NMA resin. We will consider in detail the case of Rexyn 203. From Fig. 5, we see that the effluent nitrate-ion concentration is appreciable after the passage of only 5 bed volumes of influent. However, about 70% of the nitrate ion is taken up after this. We also see that about 25% of the influent chloride is retained by the resin. After the passage of 140 bed volumes, the effluent nitrate-ion and chloride-ion concentrations began to rise, and equaled those of the influent after 220 bed volumes.

In this experiment, 220 bed volumes of influent corresponds to an input of 154 meq of chloride ion and 31 meq of nitrate ion (a total of 185 meq). From the analysis of the effluent, we found that 123 meq of chloride ion and 11 meq of nitrate ion had passed through the column, which corresponds to 31 meq of chloride ion and 20 meq of nitrate ion (a total of 51 meq) taken up by the resin. This, however, is 20 meq greater than the total capacity of the resin in the column. We have no explanation for this.

More important than the above discrepancy is the behavior of the resin in its free-base form. Fig. 7 shows the change in effluent pH as a function of the number of bed volumes of effluent. We see that the pH remains between 8 and 9 until the nitrate-ion and chloride-ion concentrations of the effluent begin to increase (after the passage of 140 bed volumes). Let us examine what is occurring in these first 140 bed volumes.

Since the influent pH = 2 (0.01M in hydrogen ion), and since the effluent pH is between 8 and 9, we can say that virtually all of the hydrogen ion is being removed from the influent by the resin. For 1 bed volume, this corresponds to 0.25 meq of hydrogen ion. From the differences in the chloride-ion and nitrate-ion concentrations in the influent and effluent, it is found (within experimental error) that, for 1 bed volume, 0.25 meq of mixed anions is retained. Therefore, we see that the resin takes up the same number of anions as hydrogen ions. That is, anions are only retained when the hydroxide form of the resin is being neutralized (or the free-base form is converted to the ammonium form) by hydrogen ion. This is expected for a normal, weak-base resin, such as Rexyn 203. However, this places a severe limitation on the resin since the influent pH limits the number of anions that the resin can retain. This limitation apparently does not apply to the 1-NMA resin.

We then set up experiments to determine the material balance with the three resins used for the breakthrough experiments (reported above). Regeneration was carried out by treating each resin column with

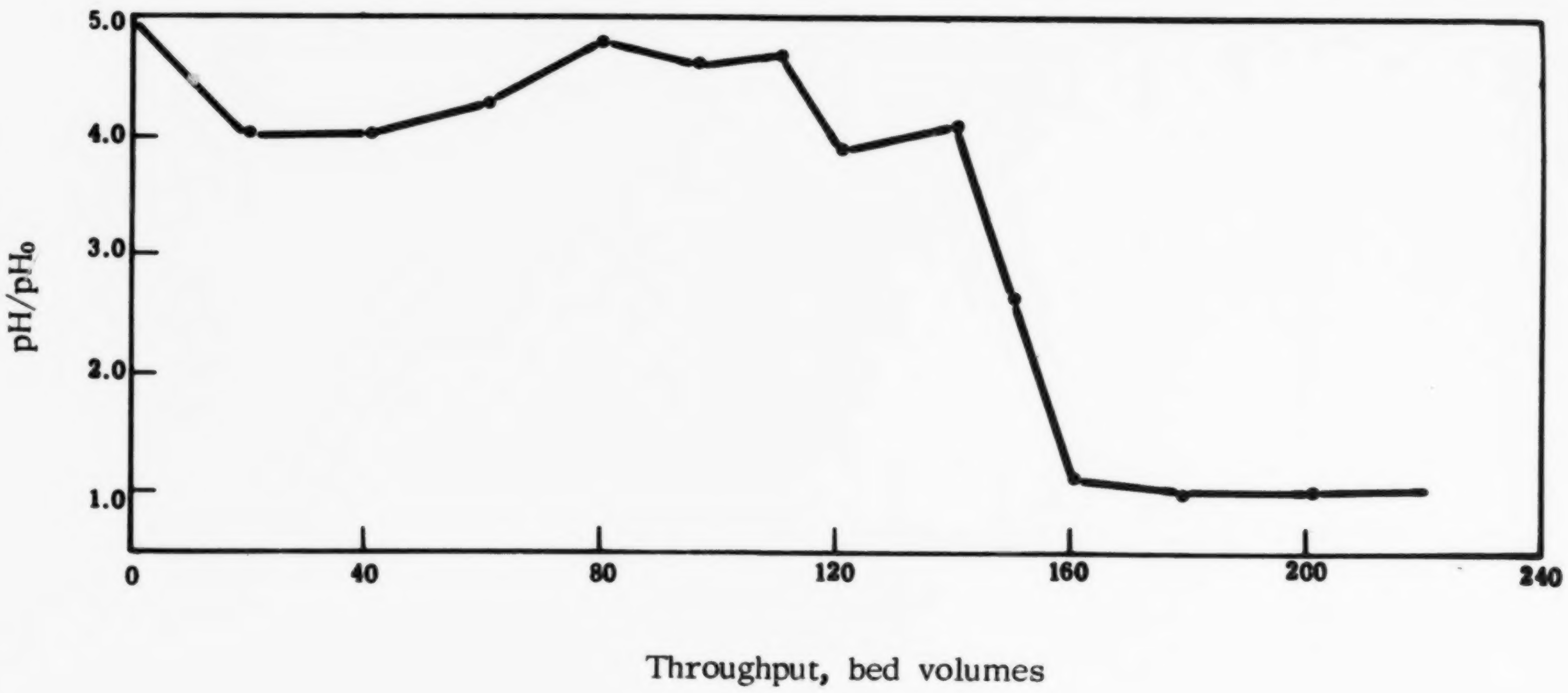


Fig. 7. Ratio of effluent pH to influent pH (pH/pH_0) as a function of throughput (in bed volumes) for Rexyn 203

a known volume (greater than 500 ml) of 1.25M NaOH solution. The NaOH wash solution was neutralized with a known amount of 1N H_2SO_4, and then it was analyzed for nitrate and chloride ions. The results, for the material balance, are given in Table XI.

Table XI. Material Balance on Regeneration Effluents

Resin	Observed* Quantity of Ion, meq		Calculated† Quantity of Ion, meq	
	Nitrate	Chloride	Nitrate	Chloride
1-NMA	2.5	0.90	8.5	—
Rexyn 203	18.0	14.8	20.0	31.0
Duolite A7	15.0	22.0	19.0	36.5

---

* Determined from regeneration.

† Determined by the difference in influent and effluent concentrations.

If we consider the results for the 1-NMA resin, we see that it must have retained only a very small amount of chloride ion since only 0.90 meq of chloride ion was found in the effluent after regeneration. This is to be expected since the resin actually gave up chloride ion during the breakthrough experiment (as evidenced by the fact that chloride ion had been displaced by nitrate ion). The quantity of nitrate ion recovered was considerably less than that adsorbed. Although the resin had taken up 8.5 meq of nitrate ion during the breakthrough experiments, upon regeneration, 2.5 meq of nitrate was found in the effluent. This suggests that the affinity of the resin for nitrate is so high that regeneration is inordinately difficult: the selectivity of the resin for nitrate is too high.

The results of the material balance for Rexyn 203 and Duolite A7 are again similar to each other, but quite different from the 1-NMA resin. We will consider in detail the case for Rexyn 203. We see, from the data in Table XI, that the amount of nitrate ion released upon regeneration corresponds very closely to the amount of nitrate ion initially taken up. In the case of chloride ion, we find that the effluent, after regeneration, contains only 14.8 meq which is significantly smaller (31.0 meq) than that originally retained by the resin. This severe discrepancy is perhaps due to small errors inherent in the analysis of influent and effluent, spread over a large volume of treated water. Furthermore, the apparent uptake was considerably higher than the known capacity of the resin.

Following the regeneration of the above three resin columns, each column was washed with 100 mg/l sodium chloride solution until the effluent was neutral. The resins were again subjected to an aqueous influent, at pH = 2.6, containing 25 mg/l (4.03×10^{-4} M) of nitrate ion and 100 mg/l (2.82×10^{-3} M) of chloride ion. The flow rate was 1.5 gal./min/cu ft. The sizes of the columns were the same as reported before. Although the results of these breakthrough experiments are not complete, one important fact may be noted. The 1-NMA resin now showed little capacity for absorption of either nitrate ion or chloride ion. In fact, after a throughput of only 10 bed volumes, the influent and effluent solutions were identical in both chloride-ion concentration and pH. After a throughput of 102 bed volumes, the influent and effluent nitrate-ion concentrations were also equal. During this period, the influent nitrate-ion concentration had been reduced only by approximately 20%, which corresponds to an uptake of only 0.1 meq of nitrate ion. These results appear to confirm the previous observation that the resin was not regenerated.

In another set of experiments, we studied the breakthrough characteristics of the three resins in their hydrochloride form. The influent, in this case, was an aqueous solution containing 100 mg/l (1.61×10^{-3} M) of nitrate ion and 291 mg/l (8.2×10^{-3} M) of chloride ion at pH = 2. The flow rate was 1.1 gal./min/cu ft. The physical properties of each column are given in Table XII.

Table XII. Physical Properties of Resin Columns

Resin	Total Capacity, meq *	Height, cm	Ratio of Height to Diameter
1-NMA	18	8	4
Rexyn 203	30	8	4
Duolite A7	50	8	4

---

* Calculated from capacity in meq/g.

Figs. 8, 9, and 10 show the ratio of effluent concentration to influent concentration, C/C_0, as a function of throughput (in bed volumes) for the 1-NMA resin, Rexyn 203, and Duolite A7 in their hydrochloride form.

In the case of the 1-NMA resin, it may be seen, from Fig. 8 that the influent nitrate-ion concentration is reduced to 10% of its initial value up to a throughput of 180 bed volumes. Thereafter, the effluent nitrate-ion concentration gradually increases until it equals that of the influent after a throughput of 320 bed volumes. At the same time, the effluent chloride-ion concentration is greater than that of the influent. From an analysis of the effluent, it was determined that the resin retained 8.5 meq of nitrate ion, but gave up 25.5 meq of chloride ion. Thus, the resin appears to release chloride ion over and above that which is replaced by nitrate ion. We could conclude that the resin is an extremely weak base, being hydrolyzed even at $pH = 2$.

The results for Rexyn 203 and Duolite A7 are more conventional. We will consider only the case of Rexyn 203. From Fig. 9, we see that the influent nitrate-ion concentration is reduced by about 90%, to a level of about 12 mg/l, up to a throughput of 320 bed volumes. After this, the amount removed decreases until the influent and effluent concentrations are equal (after a throughput of 520 bed volumes). The effluent chloride-ion concentration is again higher than that of the influent during this period. From the influent and effluent concentrations, we find that the resin retains 15 meq of nitrate ion, but gives up an excess of 27.6 meq of chloride ion.

The above observation, that more chloride ion was released than nitrate ion was absorbed, may not be completely valid since the weak-base resins are extremely difficult to wash. Rexyn 203 has a strong tendency to hydrolyze in water. Thus, although we wash the resin with a large quantity of dioxane, we are never certain that all regenerant solution has been removed. The discrepancy between observed and calculated concentrations of chloride ion found, for Rexyn 203 and Duolite A7 (Table XI) in this last set of experiments, could conceivably be explained on this basis, but the discrepancy for 1-NMA appears inordinately high.

REGENERATION EXPERIMENTS
(SEPTEMBER — DECEMBER 1969)

It was stated earlier that the loss of ion-exchange capacity by the 1-NMA resin could have been due to deterioration of the resin or to the inability to regenerate it. In determining the capacity of the same batch of resin, we subjected it to several ion-exchange/regeneration cycles. These results are described below.

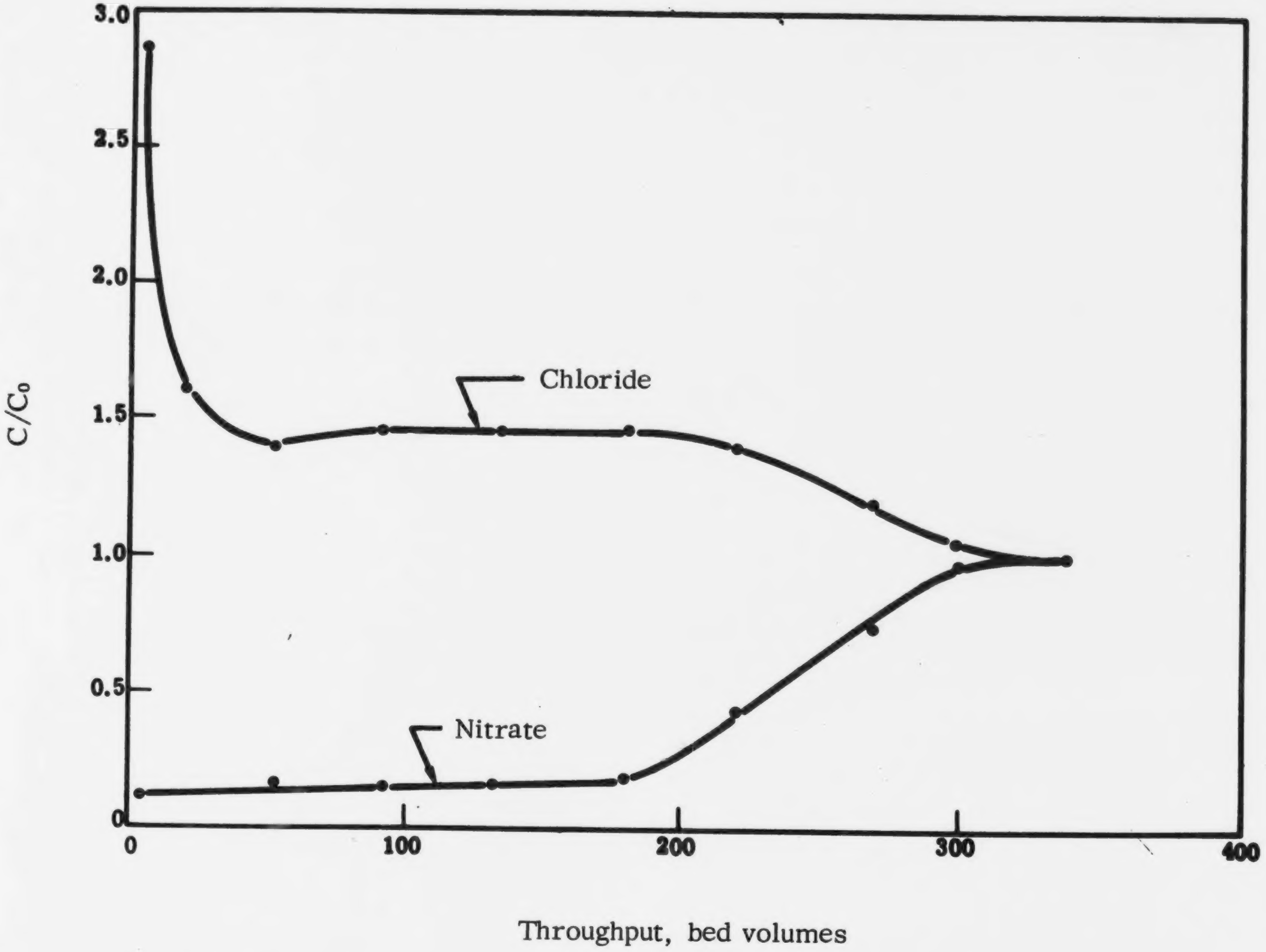


Fig. 8. Ratio of effluent concentration to influent concentration, C/C_0, as a function of throughput (in bed volumes) for the 1-NMA resin (influent contains 0.00161M nitrate ion and 0.0082M chloride ion)

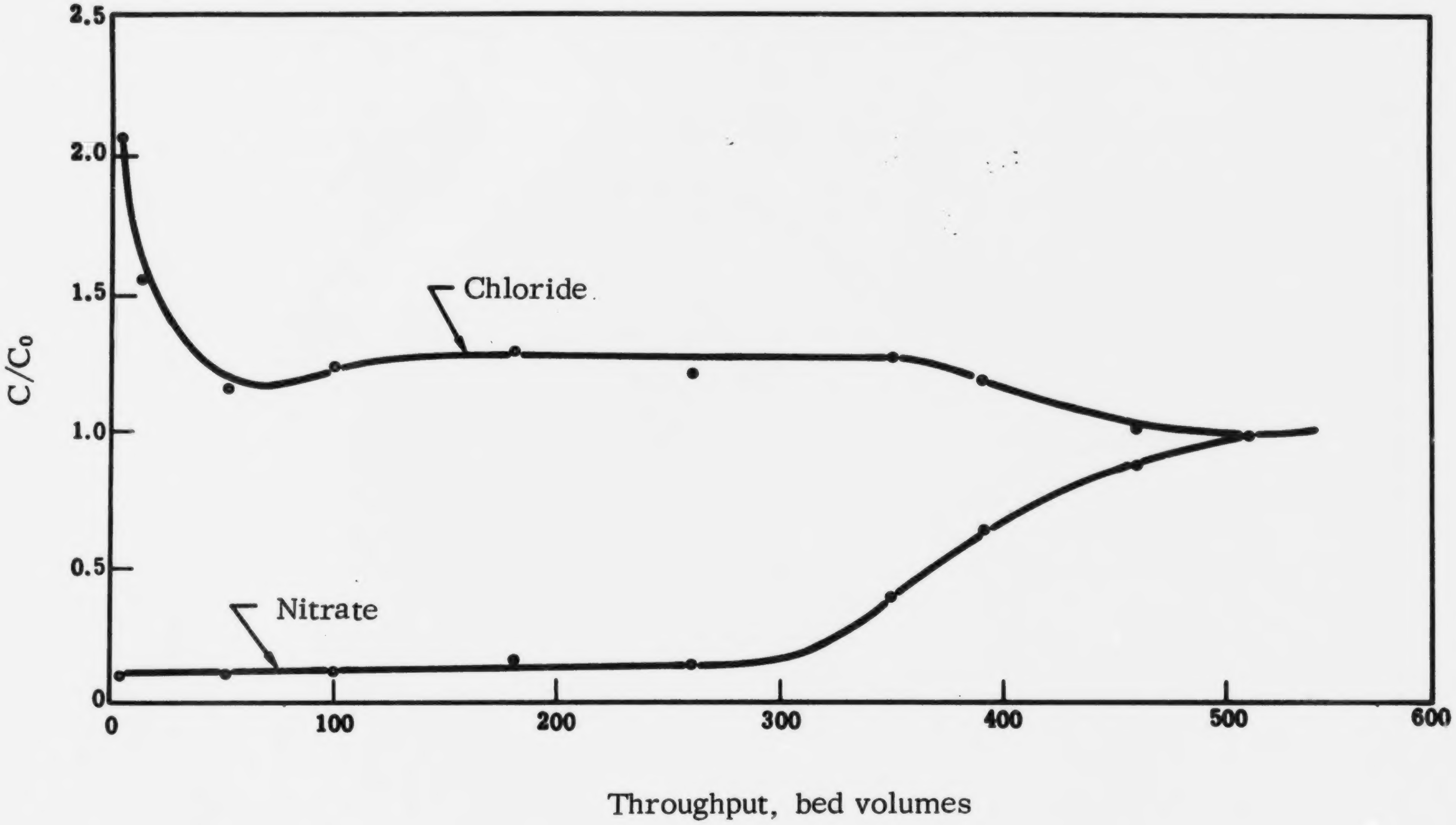


Fig. 9. Ratio of effluent concentration to influent concentration, C/C_0, as a function of throughput (in bed volumes) for Rexyn 203 (influent contains 0.00161M nitrate ion and 0.0082M chloride ion)

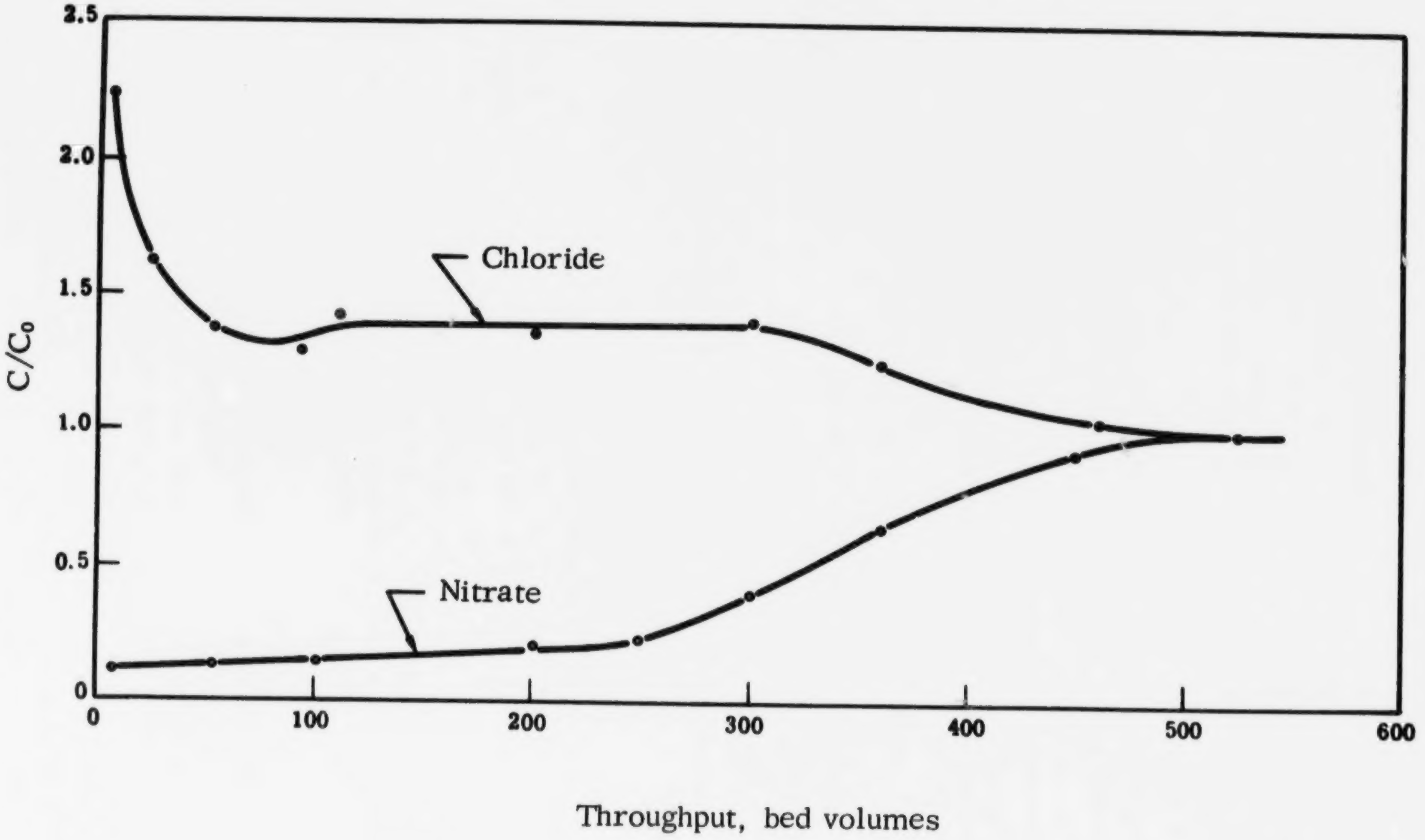


Fig. 10. Ratio of effluent concentration to influent concentration, C/C_0, as a function of throughput (in bed volumes) for Duolite A7 (influent contains 0.00161M nitrate ion and 0.0082M chloride ion)

Four grams of the 1-NMA resin, in its free-base form, was placed in a 1.4-cm-diameter column (the height of the resin was 4.5 cm). The resin was initially treated with 500 ml of 3M HCl to convert it into its hydrochloride form. The column was then washed with 45 ml of water to remove residual hydrochloric acid. After the column had been treated with 500 ml of 1.25M NaOH, the effluent was neutralized with sulfuric acid. Analysis of the total chloride-ion concentration (with the Orion chloride-ion electrode) showed that the capacity of the resin was 0.18 meq/g. This value was very much lower than that expected from our previous capacity determinations.

The 1-NMA resin was then washed with 200 ml of H_2O, followed by treatment with 590 ml of 3M HNO_3. After washing with 85 ml of H_2O, the column was washed with 1 l of 1.25M NaOH. Analysis of the NaOH wash for total nitrate-ion concentration (with the Orion nitrate-ion electrode) showed that the capacity of the resin was 0.14 meq/g. Again, this value is very much lower than expected. It was suspected that washing with water, to remove residual HCl or HNO_3, was also hydrolyzing the weak-base resin, and therefore its capacity had been greatly reduced.

Consequently, the following procedure was utilized to determine the capacity. The resin was washed with 200 ml of H_2O, followed by 500 ml of 1.25M hydrochloric acid. However, to prevent ion loss, the column was then washed with 40 ml of 1, 4 dioxane. This was followed by 1,118 ml of 1.25M NaOH. Analysis for total chloride ion resulted in a capacity of 0.65 meq/g which is much larger than that obtained above (yet still considerably lower than expected).

Again, the resin was treated with water, hydrochloric acid, and dioxane, as above. However, it was then treated with 475 ml of $NaNO_3$, and the total chloride-ion concentration was determined. The capacity in this case was 1.51 meq/g which is near the value expected. It appears that chloride ion is more easily displaced by nitrate ion than by hydroxide ion; i.e., the resin is more selective for nitrate ion than hydroxide ion. This also shows that, for a very selective resin, one must be careful in the choice of methods (1) for determining the resin's capacity, and (2) for regeneration.

Following the $NaNO_3$ wash, the resin was treated with 500 ml of 3M HNO_3, and 50 ml of 1, 4 dioxane. Treatment with 1,080 ml of 1.25M NaOH, and analysis for total nitrate ion, gave a value of 1.3 meq/g for the capacity. This value is reasonably close to that obtained using a $NaNO_3$ wash.

The resin was again treated with H_2O, HCl, and dioxane, as above, followed by washing with NaOH and analyzing for total chloride ion. The capacity in this case was 0.75 meq/g, very close to the value we had obtained above by the same procedure, but again lower than expected. The capacity of the resin was again determined, using a $NaNO_3$ wash. In this case, a value of 1.1 meq/g was obtained. This value is somewhat lower than the value obtained previously by the same method.

Although a complete material balance was not determined for the above cycling of the 1-NMA resin, several important observations can be made. First, we have seen that the resin can be subjected to several ion-exchange/regeneration cycles without a great deal of deterioration. In the final sequence, when the capacity was somewhat lower than that obtained previously by the same method, we may be observing some deterioration after seven cycles. Second, the various capacities obtained by the different methods show that it is imperative to develop an optimum method for the regeneration of the resin. In the case of the 1-NMA resin, which is very selective for nitrate ion, it would be advisable to convert the resin first to its hydrochloride form, then to displace the chloride ion with nitrate ion, as we have done. Also, the usual order of ion selectivities for weak-base resins does not hold in the case of the 1-NMA resin. That is, the resin appears to be somewhat more selective for nitrate ion than for hydroxide ion.

Work continued in an effort to find an acceptable regeneration procedure for the synthetic, 1-NMA, ion-exchange resin. While the resin samples were subjected to these recycling procedures, careful analysis permitted complete material balances to be made, thus verifying the adsorption and regeneration data. In the first study, a new batch of 1-NMA resin was prepared, and 2.95 g of the material was placed in a 9-mm-diameter column (the height of the resin was 65 mm). The material was washed with 250 ml of 1N HCl, followed by 25 ml of dioxane to remove residual HCl. The resin was then treated with 550 ml of 0.113N HNO_3. After the effluent had been neutralized, analyses for nitrate ion and chloride ion (with Orion specific-ion electrodes) revealed that 4.8 meq of nitrate ion had been retained by the resin, while 4.9 meq of chloride ion was released. This excellent agreement established the fact that the nitrate ion was replacing the chloride ion quantitatively.

After the nitric acid treatment, the resin was washed with 25 ml of dioxane to remove the excess nitrate solution. Regeneration was then attempted by treatment with 420 ml of 1M NH_4OH. Nitrate analysis of the effluent at various intervals showed that 2.8 meq of nitrate ion was released in the first 100 ml of effluent, while the next 320 ml of wash solution contained less than 0.1 meq of nitrate ion. Since the amount of nitrate ion released did not correspond to the amount retained by the resin during the nitric acid treatment, the resin was subjected to regeneration with stronger bases. The resin was treated successively with 182 ml of 1M sodium bicarbonate, 90 ml of 1M sodium carbonate, and 100 ml of 1.25M sodium hydroxide. Analysis of the effluent after each wash revealed that very small amounts of nitrate ion had been removed from the resin, but the total did not exceed 0.05 meq. Thus, although the resin had apparently taken up 4.8 meq of nitrate ion, only 2.9 meq was recovered by alkaline regeneration. It would appear that an appreciable amount of nitrate ion was irreversibly bound to the resin, as far as standard regeneration methods were concerned.

Since the resin had released a considerable amount of nitrate ion, we attempted to determine if the resin had the capacity to adsorb nitrate again. Treatment of the resin with 125 ml of 0.113N HNO_3 disclosed that 3.3 meq of nitrate ion was retained in this second adsorption cycle. Although this value is somewhat larger than the amount released in the regeneration step, the figure is reasonable.

Regeneration was again attempted by washing with 168 ml of 1.25M sodium hydroxide. This resulted in the recovery of 0.03 meq of nitrate. Further treatment with 153 ml of 1M ammonium hydroxide produced only an additional 0.4 meq of nitrate ion. Again, the amount of nitrate ion removed was significantly smaller than the amount adsorbed.

It is not completely clear why this loss in activity is taking place, although some reasons can be presented to guide future work. First, the reduction in activity of this resin seems to have occurred because nitrate ion could not be removed, rather than because of destruction of the resin sites. This leaves the possibility that more rigorous regeneration methods could recover the usefulness of the resin. On the other hand, there may be a difference, in the absorption mechanism, between the resin in the hydrochloride form and in the free-base form. Sodium hydroxide may have affected the resin during the regeneration step, and may have altered the absorption site to the point where newly-bound nitrate cannot be removed. Other experimental results tend to support this conclusion, but the evidence is not strong enough to confirm the hypothesis. More work should be done in these areas to confirm or reject these ideas.

In another set of recycling tests, three columns of freshly prepared, 1-NMA resin were set up, each containing 1 g of resin. The first column was washed with 25 ml of dioxane, followed by treatment with 76 ml of 0.1M sodium nitrate. Analysis of the effluent showed that 0.6 meq of nitrate ion was retained, while 2.6 meq of chloride ion was released. The second column was first washed with 100 ml of 1M HCl before the treatment with the 25 ml of dioxane and 75 ml of 0.1M sodium nitrate. The effluent analysis showed adsorption of 0.5 meq of nitrate ion, while 1.2 meq of chloride ion was released. The third column was treated with 75 ml of 1.25M sodium hydroxide. Analysis of the effluent showed that 2.5 meq of chloride ion was released.

This last result is quite reasonable since it shows the release of an amount of chloride ion approximately equal to the theoretical capacity of the resin. The first two tests are harder to explain since it appears that more chloride ion was released from the resin than was replaced by nitrate ion. However, examination of the method by which the resin is prepared sheds some light on the problem.

When the 1-NMA resin is synthesized, a 20:1 excess of the primary amine is used. It is possible that this free primary amine is more reactive than the secondary amine of the resin and tends to remove the HCl from the resin(thus forming free, amine hydrochloride). If this free amine hydrochloride is not completely washed out after the synthesis is complete, it will still be in the resin when the column is prepared. During the acidic washings, the amine hydrochloride can be removed from the resin, thereby showing a disproportionate amount of chloride ion in the effluent.

This hypothesis was verified by washing another batch of the same resin with 25 ml of 0.1M HCl and analyzing the effluent for chloride ion. The effluent was found to contain an excess of chloride ion which established that some source of freely mobile chloride ion must exist in the resin. This condition should not reduce the activity of the resin since all free chloride ion must have come from the reaction of amine with chloromethylated polystyrene to form the 1-NMA resin. The only difference is that the resin would then be in the free-base form, rather than in the hydrochloride form, which may result in somewhat different, ion-exchange properties.

Emphasis was next placed on the development of techniques for regenerating the 1-NMA resin. Previous work centered on the use of strongly and weakly basic solutions to regenerate the resin since this resin should be readily converted to the free-base form by basic solutions.

The previous attempts at regeneration were only partly successful, and the data were highly erratic. We concluded that the difficulty in regenerating the resin is related to the low degree of swelling of the resin and its inherent hydrophobicity, both of which make it accessible to aqueous solutions only with difficulty. It appears that the resin, at best, swells relatively little, and that the degree of swelling is strongly dependent on both the ionic strength and the pH of the aqueous solution in contact with the resin. Therefore, small changes in solution composition may cause large changes in the rate of the exchange reaction.

For this reason, we attempted regeneration with dilute hydrochloric acid. It was believed that the resin would thereby be maintained in the salt form and be reasonably swollen. Furthermore, in order to expedite the work, the regenerated resin was reacted with dilute nitric acid solutions (0.1N), instead of with simulated wastewater. The reason for this change was to reduce the time for an exchange cycle: if a simulated wastewater containing 100 mg/1 (1.6 meq/1) nitrate is passed through a 4-g column of resin (1.75 meq/g capacity), approximately 4.6 l of solution is required to spend the resin completely, assuming that all nitrate ion is removed. We have discovered that, because of the small particle size of the 1-NMA resin, it may take 2 to 3 days to pass that much solution through the column. With 0.1N nitrate solutions (100 meq/l), the minimum quantity of solution required is only about 150 ml, and the cycle time can be minimized.

The series of exchange/regeneration cycles was carried out with a resin column containing 4 g of 1-NMA resin. A quantity of 0.1N HCl was passed through the column, followed by a small quantity of water to remove residual, interstitial HCl. Nitrate adsorption was evaluated by eluting the column with 0.1N HNO_3. The column was again washed with a small quantity of water, after which the resin was regenerated with 0.1N HCl. This procedure was followed for several cycles, as shown in Table XIII.

The prior history of this resin sample involved several nitrate-uptake/regeneration cycles in which capacities ranging from 1.2 to 1.5 meq/g were observed. Regeneration with 5% NaOH was quite erratic, and HCl treatment was generally more successful. Just prior to the beginning of the experiments in Table XIII, the resin, in the hydrochloride form, had been treated with 900 ml of 1N $NaNO_3$ solution, during which 1.2 meq/g of Cl^- was released.

The 4-1/2 exchange cycles shown in Table XIII generated a good deal of data which shed light on the behavior of the 1-NMA resin as a selective, nitrate-ion exchanger. The following discussion is intended to clarify the points made by the data, as well as to establish guides for future work.

The sample of 1-NMA resin used was made from an intermediate containing 73.6% chloromethylated polystyrene (remainder: polystyrene). If reaction with 1-naphthylmethylamine had been complete, the calculated capacity would have been 2.75 meq/g. The resin was first washed extensively with HCl and showed an uptake of 1.1 meq/g of chloride ion, approximately equal to the previous adsorption of nitrate ion. The water wash removed 0.30 meq/g of chloride ion (or 1.2 meq total) in such a manner as to show that water alone removed chloride ion from the ion-exchange sites very slowly. The 50 ml of water wash was analyzed every 10 ml, and the analysis showed a high chloride-ion concentration in the first 20 ml which dropped off very suddenly to a low, constant level in the last 30 ml. It is apparent that the original, high, chloride content was due to the residual hydrochloric acid, and the lower plateau resulted from the slow hydrolysis of the ion-exchange sites. From the shape of the resulting wash curve, it was decided that subsequent water washings would consist of 25 ml of water.

Table XIII. Acid-Exchange Cycles of 1-NMA Resin

Treatment No.	Column Feed[*]		Ion Uptake		Ion Release	
	Species	ml	Species	meq/g	Species	Meq/g
1	HCl	790	Cl^-	1.6	NO_3^-	3.48[†]
2	H_2O	50	—	—	Cl^-	0.30[‡]
3	HNO_3	175	NO_3^-	1.60	Cl^-	1.91
4	HCl	100	Cl^-	0.69	NO_3^-	0.97[†]
5	H_2O	25	—	—	Cl^-	0.17
6	HNO_3	125	Not determined		Cl^-	0.92
7	H_2O	25	—	—	NO_3^-	0.20
8	HCl	100	Cl^-	0.61	NO_3^-	0.74
9	H_2O	25	—	—	Cl^-	0.26
10	HNO_3	100	NO_3^-	0.77	Cl^-	0.93
11	H_2O	25	—	—	NO_3^-	0.14
12	HCl	100	Cl^-	0.69	NO_3^-	0.58
13	H_2O	25	—	—	Cl^-	0.16
14	HNO_3	125	NO_3^-	0.68	Cl^-	0.84
15	H_2O	25	—	—	NO_3^-	0.16
16	HCl	100	Cl^-	0.80	NO_3^-	0.69

---

[*] All acid wash solutions were 0.1M

[†] In the absence of a preceding water wash, ion release includes residual, interstitial solution from the previous treatment. In treatment no. 1, this value is significant since the prior treatment had been with 1N $NaNO_3$.

[‡] The "ions released" value in a water wash is expressed as meq/g and is probably attributable to residual, interstitial solution from the prior treatment, although some hydrolysis of the weak-base group may be occurring. The sum of these two values is generally small compared to the capacity.

The 1-NMA resin was then contacted with 175 ml of nitric acid (wash treatment no. 3) and showed an uptake of 1.60 meq/g of nitrate ion. That this is larger than the original chloride uptake is not surprising since there must have been a residual capacity in the resin from previous washings. In general, the ion uptake for each treatment should equal the release of the other anion from the resin, and this is roughly true for most of the tests shown. Some transient difficulty was encountered from time to time in the operation of the chloride electrode, and, in general, the nitrate values were more dependable.

It is interesting to note that a total material balance on the two ions throughout the entire series of tests (starting with the resin in the hydrochloride form after wash no. 1) showed that the chloride-ion uptake was 2.79 meq/g, and the chloride-ion release was 5.49 meq/g; while the nitrate-ion uptake was 3.85 meq/g (assuming about 0.80 meq/g uptake in test no. 6), and the nitrate-ion release was 3.48 meq/g. It would appear that, during the exchange reaction, the resin was gradually hydrolyzing to the free-base form. The nitrate-ion material balance was much closer, indicating that it was more difficult to hydrolyze the bound nitrate than the bound chloride (which presents further evidence of the resin's nitrate-specificity).

It seemed apparent from the data that the 1-NMA resin does not readily give up its ions. The first wash, with 790 ml of 0.1N HCl, had apparently been sufficient to regenerate the resin to the hydrochloride form completely because, in the subsequent treatment (no. 3) with 0.1N nitric acid, a capacity in the region of 1.60 to 1.91 meq/g was exhibited. Subsequent regeneration (no. 4), with 0.1N HCl (100 ml), appeared to liberate less than half of the available exchange sites.

The chloride-ion uptake value of 0.69 meq/g indicated that the resin had been only about 45% regenerated in treatment no. 4. Subsequent exposure to nitrate ion (no. 6) completely exhausted the resin. Subsequent regeneration treatments (nos. 8, 12, and 16) released only 40% to 50% of the active sites which resulted in corresponding capacities for nitrate in treatments nos. 10 and 14. The regeneration treatments were insufficient since the last volume of HCl solution in each case liberated a significant quantity of nitrate ion. This is shown in Table XIV (in which treatment no. 16 is detailed).

In treatment no. 16, the release of nitrate ion corresponds to 0.7 meq/g: about 40% of the available capacity. It should be noted that the addition of HCl in the last 25-ml increment was still releasing nitrate ion at a high rate. This is discussed below.

Table XIV. Regeneration of Spent 1-NMA Resin With HCl (Compare With Treatment No. 16, Table I)

Regenerant HCl (0.093N)			
Volume, ml	Cl^-, meq	Cl^- Uptake, meq	NO_3^- Release, meq
25	2.32	1.13	0.93
25	2.32	0.83	0.83
25	2.32	0.69	0.57
25	2.32	0.56	0.45
100	9.28	3.21	2.78

The ability of the 1-NMA resin in the hydrochloride (or salt) form to exchange with neutral, nitrate-ion solutions was demonstrated in a further series of experiments summarized in Table XV

Table XV. Nitrate-Ion Uptake From Neutral Solutions (Continuation of Table I Experiments)

	Column Feed		Ion Uptake		Ion Release	
Treatment No.	Species	ml	Species	meq/g	Species	meq/g
17	3N HCl	100	—	—	—	—
18	0.1N HCl	100	—	—	NO_3^-	0.10
19	H_2O	55	—	—	Cl^-	0.43
20	0.1N $NaNO_3$	125	NO_3^-	1.3	Cl^-	0.90
21	H_2O	25	—	—	NO_3^-	0.16

With a weak-base resin, two possible reactions are expected in an exchange with a neutral solution:

$$RNH_2^+Cl^- + NO_3^- \rightarrow RNH_2^+NO_3^- + Cl^-$$

and

$$\dot{R}NH_2^+Cl^- + H_2O \rightarrow RNH \cdot H_2O + Cl^- + H^+$$

The first reaction is known to be rapid, whereas the second is generally slow. The data of Table XV indicate the ability of the 1-NMA resin, in the hydrochloride form, to convert to the hydronitrate form more rapidly than to hydrolyze to the free-base form, under the conditions of the experiment. The relative rates are expected to change markedly in solutions containing much lower concentrations of nitrate ion in neutral solutions.

Based on the previously discussed decision to try a lower degree of cross-linking in the polymer, experiments were run using 1%-DVB-cross-linked polystyrene to produce a new batch of 1-NMA resin. The resin was used in several cycles of nitrate absorption and HCl regeneration. Solutions used in these experiments were neutral, dilute mixtures of nitrate and chloride ions, approximating the concentrations found in wastewater.

The initial series of regeneration tests used 0.1N $NaNO_3$. The results are shown in Table XVI. It is significant that the resin maintained its capacity throughout the series of cycles.

A series of breakthrough experiments was also run, using both the 1-NMA resin (1% DVB) and the commercial resins, Rexyn 203 and Duolite A7. The nitrate-ion solution to be run contained 25 mg/l nitrate ion and 100 mg/l chloride ion. The results of these tests are shown in Table XVII. Note that the new resin achieves 81.5% nitrate-ion removal, compared to 58% for the commercial resins. These data clearly show that, although the capacity of the 1-NMA resin is lower than the commercial resins, the new material is capable of producing a much cleaner effluent.

Table XVI. Acid Regeneration of 1-NMA Resin Prepared From 1% DVB-Cross-Linked Polystyrene

Treatment No.	Column Feed		Ion Uptake		Ion Release	
	Species	ml	Species	meq/g	Species	meq/g
1	H_2O	250	—	—	—	—
2	HCl (3N)	100	—	—	—	—
3	HCl (1N)	100	—	—	—	—
4	H_2O	25	—	—	—	—
5	$NaNO_3$	100	NO_3^-	1.40	Cl^-	1.60
6	H_2O	25	—	—	NO_3^-	0.39
7	HCl (1N)	100	—	—	—	—
8	H_2O	50	—	—	—	—
9	$NaNO_3$	100	NO_3^-	1.40	Cl^-	1.38
10	H_2O	40	—	—	NO_3^-	0.37
					Cl^-	0.02
11	HCl (3N)	100	—	—	—	—
12	HCl (1N)	25	—	—	—	—
13	H_2O	25	—	—	Cl^-	0.73
					NO_3	0.01
14	$NaNO_3$	100	NO_3^-	1.35	Cl^-	1.61
15	H_2O	25	—	—	NO_3	0.43
16	HCl (3N)	100	—	—	—	—
17	HCl (1N)	25	—	—	—	—
18	H_2O	25	—	—	Cl^-	0.80
					NO_3^-	0.01
19	$NaNO_3^-$	100	NO_3^-	1.36	Cl^-	1.63
20	H_2O	25	—	—	NO_3^-	0.43
					Cl^-	0.01

Table XVII. Breakthrough Experiments: 1-NMA Resin (1% DVB), Rexyn 203, and Duolite A7

	1-NMA	Rexyn 203	Duolite A7
Total solution used up to breakthrough point, ml	3877	9325	9525
NO_3^- uptake, meq/g	0.423	0.510	0.546
Cl^- release, meq/g	1.15	2.26	3.29
NO_3^- removed, %	81.5	58.2	58.0

★ U. S. GOVERNMENT PRINTING OFFICE : 1970 O - 409-233